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THERMAL CONDUCTIVITY OF CARBON AND GRAPHITE CLOTHS PHENOLIC AT 100 TO 1100°C

by

Elder H. Bartel
Propulsion Development Department

ABSTRACT. Thermal conductivity values of fabric-reinforced laminates are reported for virgin and charred laminates. Data are presented graphically from 100 to 1100°C. Two types of graphite cloth and two types of carbon cloth were investigated as laminate reinforcements at angles of 0 and 90 degrees to heat flow direction. Parameters of molding pressure, char temperature, and additional orientations at 30 and 60 degrees were investigated for one type of laminate. Two specimens taken from a fired rocket motor ablative chamber were evaluated and compared to a laboratory counterpart.

Fabric orientation with respect to heat flow direction was found to have the greatest influence on thermal conductivity in laminates.

A discussion is presented to explain the decrease in thermal conductivity when charring of the laminate resin occurs.

A comparative cut-bar thermal conductivity apparatus was used to obtain values of thermal conductivity with a fairly high degree of confidence.

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Thomas S. Amtic, Ph.D. ..... Technical Director

FOREWORD

This report presents the results of work conducted during July 1966 to August 1968 to determine the thermal conductivity of carbon cloth phenolics from room temperature (approximately 70°F) to 1100°C. Laboratory specimen results are compared to specimens fired in an ablative rocket chamber.

The project was part of the Navy in-house effort on Advanced Liquid Engine Materials AirTask A-33-536-706/216-1/F009-06-02 to supply needed information on thermal conductivity for virgin and charred materials used in ablative chambers.

This report was reviewed for technical accuracy by J. D. Ramsdell and Pat Hall.

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CONTENTS

Figures:

Tables:

INTRODUCTION

This study was initiated because of the lack of information on thermal conductivity of virgin and charred laminates commonly used in ablative chambers and nozzles. The lack of accurate high temperature data, required for the computer program input used to calculate the thermal response of charring ablators or insulations, was especially significant (Ref. 1, 2 and 3).

Determination of thermal conductivity is a time consuming process when accuracy is desired. Therefore, the study was limited to two types of graphite cloth and two types of carbon cloth made into laminates with phenolic resin.

The objective of this report is to provide accurate values of thermal conductivity from room temperature (approximately 70°F) to 1100°C. The upper temperature limit was imposed by commercially available equipment. Unfortunately, upper temperature limitations of 400 and 950°C were imposed for low conductivity materials by the glass and pyroceram standards which were supplied with the thermal conductivity apparatus.

Parameters investigated, which affect heat transfer, were:

1. Fiber angle
2. Molding pressure
3. Reinforcement type
4. Char temperature

Char formed in an ablative chamber was also investigated. The use of small specimens was dictated by the small size ablative chambers available.

PROCEDURE

APPARATUS

The equipment used to determine thermal conductivity is shown in Fig. 1. Model TC-200 was originally available from Minnesota Mining and Manufacturing Company in St. Paul, Minnesota where it was developed. It is now available as Model TCC GM from Dynateck Corporation. Auxiliary equipment required consisted of a voltage stabilizer, vacuum pump, sensitive potentiometer, ice bath, inert gas supply, and a constant temperature water source.

FIG. 1. Comparative Cut-Bar Thermal Conductivity Apparatus.

The apparatus is a "comparative cut-bar thermal conductivity measuring system" requiring standards (STD) of known conductivity. A specimen (Black) is shown installed in Fig. 2 between the top and bottom H standards (White) with thermocouple (TC) wires attached. The guard heater tower which contains seven heaters and seven TCs covers the top heater and is ready for lowering into position. The heat sink or bottom heater is seen at the bottom of the central column. The space between the specimen and tower guard heaters was filled with bubbled zirconia insulation after the tower was lowered. The dome was placed over the assembly (as shown in Fig. 1). The system was then evacuated, and purged three times and filled with Argon gas because oxygen in air would severely oxidize the specimens, thereby changing their properties.

Electrical power was supplied to each heater and controlled individually by the nine heater variometers, or as a group by the master control.

A reading was taken when the temperature had stabilized, between the center line of the standards and specimen and 0.8 inch outside the standards and specimen near the guard heaters, to within 1°C for two points in a plane at equal distances axially (see Fig. A1 and A2 of Appendix).

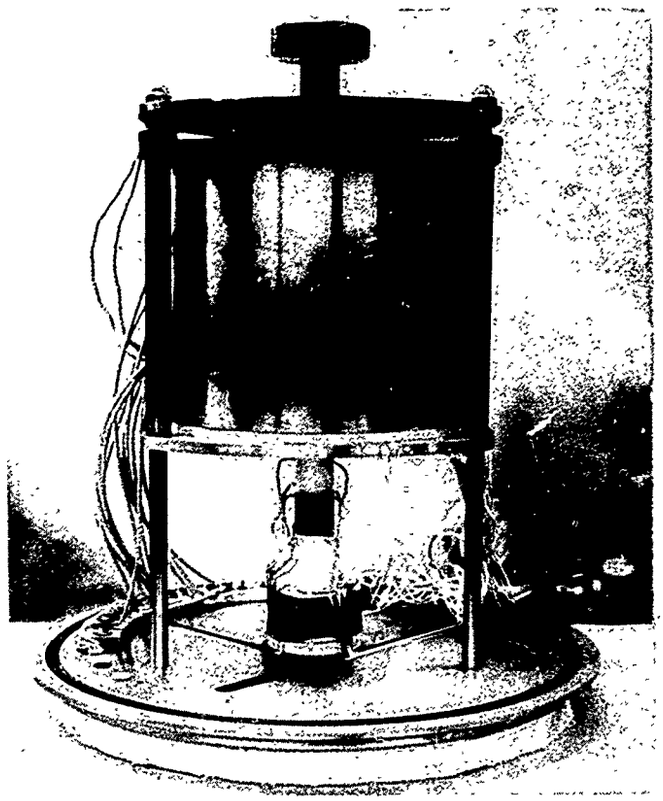


FIG. 2. Specimen, Standards, and Bottom Heater Shown with the Guard Heater Tower in the Up Position.

Thermal conductivity was then calculated using the following equation:

$$K_{specimen} = \frac{1}{2\Delta T_{sample}} \left[(K\Delta T)_{top\ standard} + (K\Delta T)_{bottom\ standard} \right]$$

Where:

K = thermal conductivity

ΔT = temperature difference between top and bottom TCs in the specimen and standards.

Allowance was made for differences in area and ΔT (see Appendix). The axial distance between top and bottom TCs was 0.75 inch for the specimen and standards (Fig. 3). Thermocouple junctions were placed on the specimen-standard center line by means of alumina insulators on the TC wires (Fig. 3). Thermocouples were .010-diameter platinum and .010-diameter platinum/10% rhodium with the appropriate lead-in wire and cold junction.

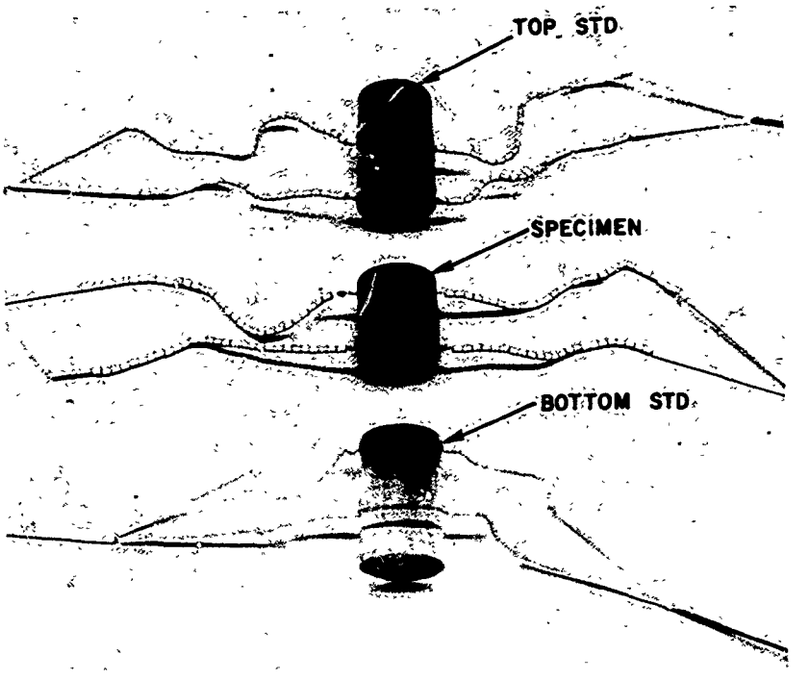


FIG. 3. Pyrex Standard G, Specimen, and Thermocouple Wires Ready for Installation.

SPECIMEN PREPARATION

All specimens were prepared by the US Polymeric Chemicals Company (USP) and were used in the as-machined condition. All specimens were right cylinders 1.000 ± 0.010-inch diameter by 1.000 ± 0.010-inch long, machined from flat fabric reinforced laminates. A typical specimen of each fiber orientation is shown in Fig. 4. All panels were molded at 1,000 psi except 1-1, 1-2, and the ablative chamber specimen, as shown in Table 1. Charred specimens were machined after charring and were given a dimensional tolerance of ±0.020 inch.

All pre-charred specimens were charred in an argon atmosphere at atmospheric pressure for a 6 hour minimum time at 816°C (1500°F), except some specimens from panel 1 were charred at 538°C (1000°F). The 6 hour time does not include furnace heat-up and cool-down time which may have been several days. All specimens of a given material were taken from a single panel (except FM 5064) to reduce molding procedure variables. FM 5064 required four panels because three molding pressures were used and the 30 and 60 degree fiber angle specimens required a thicker panel. Table 1 lists all the laminate panels used and the ablative chamber specimens prepared at NWC as well. The USP39 resin is a highly substituted ring structure phenaldehyde condensation polymer unique to USP and

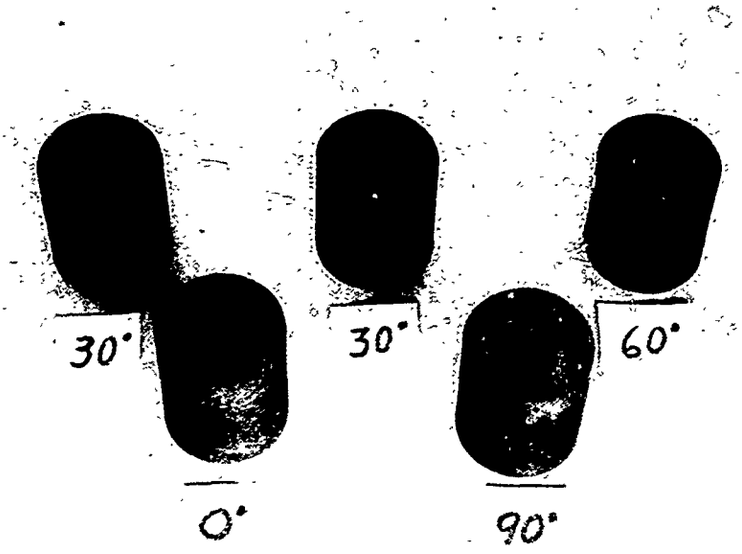


FIG. 4. Specimens of Four Fiber Orientations Were Used. The top left specimen is of two piece construction from a fired ablative chamber.

is referred to as phenolic resin in this report. The amount and type of resin filler was not given because it is proprietary to USP. Resin filler may affect thermal conductivity and definitely has an influence on the amount of pyrolysis off-gas during charring if filler is considered to be part of the resin.

Three values of resin solids are given for each panel in Table 1 under laminate properties. Resin solids by fixed carbon content method (note e) were determined by USP for each panel (test method CTM-14 of USP) by volatilizing the resin with heat and vacuum. Resin solids (note f) was obtained by subtracting the volatile and flow from the pre-preg resin content. Considerable variation exists in resin solids content by these two methods thus the averaged values give a more true resin content. Resin solids (note e) on panel 4 is exceptionally high and must be in error because the laminate should have less resin than the pre-preg due to loss by volatiles and flow, and should be closer to the value per note (f) as substantiated by weight loss on charring. The values for resin content are uncertain and difficult to determine accurately.

TABLE 1. Fabrication History of Thermal Conductivity Laminates.

	Laminate panel no.							
	1	1-1	1-2	2	3	4	7	Rocket
USP FM No.	5064	5064	5064	5164	5063	5072	5064	5064
Fabric type	WCA graphite	WCA graphite	WCA graphite	G1550 graphite	CCA1 carbon	VCK carbon phenolic	WCA graphite	WCA graphite
Resin	USP39	USP39	USP39	USP39	USP39	yes	USP39	USP39
Resin filler	yes	yes	yes	....	yes	yes	yes	yes
	PrePreg properties							
Resin content %	37.9	37.9	37.9	36.6	34.8	33.8	34.7	34.0[a]
% Volatile @ 320°F	2.45	2.8	2.45	2.21	2.03	2.34	3.1	3.5[a]
% Flow @ 325°F, 150 psi	8.1	11.9	8.1	8.65[b]	10.0[b]	19.7[b]	1.1	17.7[a]
Minutes Staging @ 200°F	140	120	140	....	120	30	120	....
	Laminate history							
Plies/1.25 inch	100	100	100	98	96	96	128	60[c]
Max. Temp. °F[d]	500	500	500	500	500	500	500	325
Max. Pressure, psi	1000	100	250	1000	1000	1000	1000	3000
Time @ max. pressure, minutes	180	180	180	180	180	180	180	30
	Laminate properties							
Resin Solids %[e]	31.7	30.55	29.9	34.41	34.41	38.87	26.62	39.2
Resin Solids %[f]	34.1	32.4	34.0	32.7	30.7	26.5	33.2	27.0
Average Resin Solids %	32.9	31.5	32.0	33.5	32.5	32.7	29.9	33.1
Specific Gravity, g/cc	1.36	1.36	1.36	1.395	1.46	1.42	1.39	1.43
Acetone Extraction, %	0	0.42	1.84	0	0	0	0	....
Specimen Fiber Orientation, degrees	0, 90	0, 90	0, 90	0, 90	0, 90	0, 90	30, 60	30
	1500°F Char Properties (816°C)							
% Weight loss	16.6[h]	16.3	16.2	16.5	16.9	13.2	16.5	18.8[g]
Specific Gravity, g/cc	1.15[i]	1.17	1.18	1.22	1.37	1.28	1.21	1.16

[a] Nominal values.

[b] At 1000 psi

[c] 60 ply per inch.

[d] Cooled under pressure and removed at room temperature.

[e] Resin solids, by fixed carbon content method.

[f] Calculated by subtracting volatile and flow from prepreg resin content.

[g] Charred in rocket motor, value calculated from density change.

[h] Specimens charred @1000°F = 15.8%.

[i] 1000°F char same as 1500°F char.

Specific gravity was determined for each virgin specimen by water immersion; the average is shown in Table 1. Charred specimens were too porous for water immersion; therefore, specific gravity was calculated from the weight, length and diameter of each specimen.

Acetone extractables give an indication of the degree of cure of the resin. The high value of 1.84 for panel 1-2 indicates that the resin in specimens of this panel may undergo further curing (cross-linking) in the thermal conductivity apparatus, though it appears not to have affected the weight loss on pre-charred specimens.

The specimen fiber orientation is the angle of the warp direction fibers in the fabric with respect to the specimen axis or heat flow direction.

The weight loss of specimens charred at 816°C (1500°F) is fairly consistent except for panel 4 where it is low. This low value is substantiated by the low resin content in the pre-preg along with the high percent resin flow in the pre-preg.

Freshly charred carbonaceous specimens have a highly active surface similar to activated charcoal, hence may pick up atmospheric moisture after being removed from the furnace. Some specimens were not used until two years after preparation and lost weight. This weight loss represents moisture picked up at USP (near the ocean) and lost at NWC (desert). Over a 1-year period, specimens charred at 816°C (1500°F) having WCA, G1550, and VCK fabrics, lost 0.24 ± 0.02g, those with CCA-1 lost 0.88g and those with WCA charred at 538°C (1000°F) lost only 0.11g. This weight change due to atmospheric moisture did not affect the thermal conductivity because absorbed water is driven off during vacuum, purging, and heating of the specimen in the thermal conductivity apparatus before a reading is taken. It is interesting to note, however, that char temperature has an effect on moisture absorption and that CCA-1 appears to be much more active in moisture absorption than the other three fabric types.

THERMAL CONDUCTIVITY DATA

Thermal conductivity data are given in Tables 2 through 9 for each specimen at each temperature evaluated. A separate table is used for each material except FM 5064 which required four tables because of the various parameters investigated such as molding pressure, char temperature, and fiber angle.

The second column gives experimental values of the thermal conductivity of the specimen in metric units. Corrected values of thermal conductivity (K) are listed in the third column. Corrected values were

TABLE 2. Thermal Conductivity of FM 5164 G1550 Graphite Cloth, USP39 Phenylaldehyde Molded at 1,000 psi.

Temp., °C	K x 10^{-4} cal / cm sec °C		Error ± %	Mismatch %	STD	Specimen no.	Weight loss %	Comments
	Exp	Corrected						
0° Orientation, Virgin								
93	113		2	+30	H	2K	30.3	
202	131		2	+57	H			Tc#4, -1.7°C off.
308	140		1	+74	H			
439	143		2	+85	H			
557	143		17	-31	C			
718	128		40	-24	C			Too low, disregard
915	160		5	+ 5	C			
1120	182		11	+31	C			
94	110		0	+27	H	2P	21.1	
202	131		0	+57	H			Tc#5, +1.3°C off.
321	137		1	+72	H			
482	167		19	-32	C			Too high, disregard
701	153		25	-11	C			
888	164		15	+ 8	C			
1135	251		1	+84	C			Too high, disregard
90° Orientation, Virgin								
92	25.3	24.4	2	-18	G	2F	9.7	
202	27.4	26.4	3	-18	G			
311	28.2	27.0	6	-22	G			
420	27.0	25.5	6	-32	G			
92	24.0	22.9	1	-22	G	2L	1.8	
205	27.0	25.9	4	-20	G			
310	27.6	26.3	7	-23	G			
0° Orientation, Charred at 1500°F								
108	112		1	+30	H	2C	13.9	
220	127		2	+53	H			
324	136		6	+70	H			
414	137		2	+76	H			
496	138		12	+84	H			
594	155		27	+115	H			
719	147		6	+107	H			
903	142		15	+112	H			
1121	138		24	+117	H			
523	150		18	-29	C			Tc#7, -1.2°C off.
710	158		24	- 7	C			
833	143		3	- 9	C			
1059	158		2	+11	C			Tc#3, +1.6°C off.
101	112		8	+30	H	2D	26.5	Delaminated by presence of oxygen*
200	128		10	+54	H			
298	138		14	+71	H			
698	161		49	+126	H			
895	140		7	+108	H			
1000	130		9	+98	H			
1091	161		23	+152	H			
915	145		14	+116	H			Decreasing temperature
542	144		2	-33	C			Tc#6, 1.4°C off.
717	106		12	-37	C			Too low, disregard
870	137		0	-11	C			
1094	146		0	+ 4	C			
90° Orientation, Charred at 1500°F								
99	31.2		6	-64	G	2A	0.3	

*Applies to all runs on Specimen 2D.

TABLE 3. Thermal Conductivity of Virgin FM 5064 WCA Graphite Cloth, USP39 Phenylaldehyde, Molded at 1,000 psi.

Temp., °C	K x 10^{-4} cal / cm sec °C		Error ± %	Mismatch %	STD	Specimen no.	Weight loss %	Comments
	Exp	Corrected						
0° Orientation								
97	84.1	83.6	0	- 3	H	1AA	17.6	Delaminated at T.C. hole*
200	95.6		1	+15	H			
311	101		1	+25	H			
407	101		2	+30	H			
608	82.5		3	+13	H			
837	85.9		18	+26	H			
100	81.1	80.0	1	- 6	H	1BB	16.3	
200	93.3		1	+11	H			
320	99.4		1	+24	H			
614	83.2		8	-12	H			
810	84.1		7	+21	H			
30° Orientation								
108	60.3	56.7	2	-30	H	7B	13.9	
212	68.1	65.6	3	-18	H			
309	71.0	69.2	1	-12	H			
394	71.6	70.5	1	- 7	H			
556	67.2	65.8	4	-10	H			
701	68.6	68.0	7	- 4	H			
898	69.3		15	+ 3	H			
102	64.0	60.7	1	-26	H	7H	6.9	
212	72.1	70.2	3	-13	H			
309	75.8	75.0	1	- 5	H			
395	77.6	77.4	1	- 1	H			
546	67.3	65.9	5	-10	H			
706	68.5	67.8	7	- 4	H			
919	67.3		9	0	H			
60° Orientation								
112	33.1	33.5	4	+ 6	G	7K	8.5	
219	36.0	36.4	13	+ 6	G			
310	37.6	38.2	7	+ 7	G			
403	32.4	30.3	22	-31.6	G			
116	34.1	34.8	5	+ 9	G	7T	8.4	
218	35.7	36.1	9	+ 6	G			
322	38.0	38.4	4	+ 5	G			
410	34.4	33.6	3	-12	G			
132	36.9	33.1	3	-57	H	7D	1	Tc#5, -2.4 °C off.
211	37.8	33.6	3	-55	H			Tc#5, +1.6 °C off.
303	40.9	37.2	2	-49	H			
90° Orientation								
98	23.7	22.6	14	-23	G	1Y		
203	25.0	23.7	10	-25	G			
94	22.4	21.2	14	-27	G			Decreasing temperature
307	24.2	23.1	2	-32	G			
91	24.1	23.0	12	-22	G	1Z	9.6	
205	25.3	24.0	9	-25	G			
308	25.8	24.4	9	-28	G			
403	24.9	23.1	4	-36	G			
308	23.5	21.9	5	-35	G			Decreasing temperature
204	23.0	21.6	8	-31	G			Decreasing temperature
100	21.0	19.7	20	-32	G			Decreasing temperature

*Applies to all runs on Specimen 1AA.

TABLE 4. Thermal Conductivity of FM 5064 Molded at 1,000 psi.

Temp., °C	K x 10^{-4} cal / cm sec °C		Error ± %	Mismatch %	STD	Specimen no.	Weight loss %	Comments
	Exp	Corrected						
0° Orientation, Charred at 1500°F								
110	87.2		3	+ 1	H	1D	7.8	
309	107		0	+32	H			
513	118		1	+56	H			
713	118		9	+66	H			
695	130		4	-24	C			
943	154		3	+ 7	C			
1110	177		9	+27	C			
111	86.4		5	+ 2	H	1H	6.2	
306	109		1	+36	H			
515	116		4	+54	H			
712	122		5	+72	H			
935	122		14	+83	H			
709	127		16	-25	C			
930	138		8	- 8	C			
1106	160		12	+15	C			
30° Orientation, Charred at 1500°F								
105	58.3	54.6	2	-32	H	7A	5.2	
309	69.3	67.4	2	-14	H			
516	78.0		1	+ 3	H			
704	82.3		4	+16	H			
896	88.5		9	+31	H			Tc#5, -1.3°C off.
102	57.0	53.4	1	-34	H	7F	7.0	
304	74.1	72.8	6	- 8	H			
509	84.1		1	+11	H			
700	85.8		5	+21	H			
902	92.6		13	+37	H			
896	92.6		9	+37	H			
60° Orientation, Charred at 1500°F								
114	29.1	28.7	3	- 7	G	7C	3.5	
219	32.6	32.4	2	- 3	G			
410	34.4	33.6	1	-12	G			
109	28.0	27.4	2	-10	G	7J	2.6	
216	31.7	31.3	1	- 6	G			
403	33.8	32.9	2	-13	G			
90° Orientation, Charred at 1500°F								
86	24.0	23.0	6	-21	G	1B	3.4	
304	29.0	27.9	0	-19	G			
417	29.1	27.6	3	-26	G			
82	24.4	23.4	3	-20	G	1J	3.4	
303	28.5	27.3	2	-21	G			
414	28.8	27.3	3	-27	G			
0° Orientation, Charred at 1000°F								
100	84.8	84.5	7	- 2	H	1A	13.5	
307	110		1	+36	H			
529	114		4	+52	H			
701	116		2	+62	H			
934	127		7	+91	H			
682	137		3	-22	C			
905	140		1	- 7	C			
1087	155		5	+10	C			
101	76.3	73.0	2	-22	H	1F	8.9	
296	96.7		2	+20	H			
537	106		1	+42	H			
684	109		2	+53	H			
944	115		5	+64	H			
691	144		1	-17	C			
933	153		1	+ 3	C			
1108	173		8	+24	C			

TABLE 5. Thermal Conductivity of FM 5064 Molded at 100 psi.

Temp., °C	K x 10^{-4} cal / cm sec °C		Error ± %	Mismatch %	STD	Specimen no.	Weight loss %	Comments
	Exp	Corrected						
0° Orientation, Virgin								
102	84.5	84.1	1	- 2	H	1-1P	19.7	
300	104		8	+29	H			
492	115		21	+51	H			
667	123		39	+71	H			Tc#1, +1.2°, #2 -1.7°C
894	143		70	+110	H			Tc#1, -1.6°, #4 -1.5°C
691	127		1	-26	C			
935	138		2	- 7	C			
1093	156		5	+11	C			
100	82.0	81.0	1	- 6	H	1-1K	20.0	
330	101		8	+26	H			
708	118		15	-31	C			
931	147		3	- 2	C			
1092	205		9	+46	C			Too high, disregard
90° Orientation, Virgin								
91	23.5	22.4	5	-23	G	1-1F	9.4	
211	28.9	28.0	4	-14	G			
312	28.0	27.6	12	-25	G			
408	27.7	26.0	5	-29	G			
87	24.1	23.5	1	-13	G	1-1L	4.2	
225	26.4	25.2	5	-22	G			
306	23.1	21.4	9	-36	G			
224	27.3	26.3	6	-19	G			Decreasing temperature
0° Orientation, Charred at 1500°F								
105	73.2	70.9	4	-15	H	1-1C	6.9	
305	91.0		2	+13	H			
521	99.1		1	+32	H			
720	102		3	+44	H			
904	101		7	+51	H			
718	108		6	-24	C			
914	119		1	-20	C			
1092	126		5	- 9	C			
107	87.1		1	+ 1	H	1-1D	19.2	
308	110		6	+37	H			
536	118		1	+60	H			
735	128		8	+81	H			
912	125		8	+86	H			
697	128		1	-26	C			
888	125		1	-18	C			
1074	130		2	- 9	C			

TABLE 6. Thermal Conductivity of FM 5064 Molded at 250 psi.

Temp., °C	K x 10^{-4} cal / cm sec °C		Error ± %	Mismatch %	STD	Specimen no.	Weight loss %	Comments
	Exp	Corrected						
0° Orientation, Virgin								
103	69.1	66.3	2	-20	H	1-2P	19.2	
317	84.0		1	+ 5	H			
503	86.8		0	+15	H			
682	95.3		7	+33	H			
882	100		8	+48	H			
920	80.3		2	-47	C			
1128	80.0		5	-42	C			
108	71.4	69.0	3	-17	H	1-2T	22.6	
316	86.4		0	+ 8	H			
491	89.0		5	+17	H			
695	101		23	+40	H			Tc#2, -2.7°C off.
879	104		18	+53	H			Tc#7, +1.2°C off.
897	81.3		3	-46	C			Too low, disregard
1101	85.5		3	-39	C			Too low, disregard
94	57.8	67.8	6	+86	G	1-2K	1.2	
209	70.6	86.4	2	+112	G			
90° Orientation, Virgin								
92	22.8	21.6	9	-25	G	1-2F	10.0	
204	30.2	29.6	7	-10	G			
310	28.8	27.6	8	-20	G			
433	28.3	26.6	8	-29	G			
82	25.4	24.5	1	-17	G	1-2L	2.6	
216	28.4	27.5	11	-16	G			
312	28.2	26.9	6	-22	G			
0° Orientation, Charred at 1500°F								
94	73.9	71.8	3	-14	H	1-2C	14.1	
300	93.9	91.0	2	-16	H			
527	10[illegible]		1	+38	H			
702	107		1	+50	H			
913	105		6	+56	H			
939	100		9	-33	C			
1096	104		6	-26	C			
103	72.1	69.8	6	-16	H	1-2D	23.4	Oxygen in system*
297	89.7		1	+11	H			
514	99.5		1	+32	H			
718	95.1		4	+34	H			
902	96.5		7	+43	H			
879	80.3		3	-48	C			Too low, disregard
1100	84.0		4	-40	C			Too low, disregard

*Applies to all runs on Specimen 1-2D.

TABLE 7. Thermal Conductivity of FM 5063 CCA-1 Carbon Cloth, USP39 Phenylaldehyde, Molded at 1,000 psi.

Temp., °C	K x 10^{-4} cal / cm sec °C		Error ± %	Mismatch %	STD	Specimen no.	Weight loss %	Comments
	Exp	Corrected						
0° Orientation, Virgin								
111	40.6	36.3	19	-53	H	3K	10.3	
217	44.0	39.8	14	-48	H			
322	47.1	43.2	7	-41	H			
416	47.1	43.4	25	-39	H			
112	31.5	31.6	1	+ 1	G	3P	8.8	
199	37.3	38.2	1	+12	G			
314	39.5	40.2	25	+ 9	G			
404	36.5	36.0	8	- 7	G			
90° Orientation, Virgin								
95	25.6	24.4	3	-23	G	3F	9.8	
202	28.6	27.8	3	-15	G			
306	29.3	28.3	6	-18	G			
404	28.7	27.2	3	-27	G			
88	23.6	22.5	1	-23	G	3L	3.0	
186	25.4	24.2	6	-23	G			
301	27.4	25.7	6	-32	G			
0° Orientation, Charred at 1500°F								
105	46.8	42.6	4	-45	H	3C	5.8	
303	59.4	56.4	1	-26	H			
521	67.4	66.1	1	-10	H			
689	71.2		1	0	H			
915	75.3		7	+12	H			
104	42.5	38.4	5	-51	H	3D	3.5	Tc#7, +1.4°C off.
310	58.1	54.8	5	-28	H			
495	64.2	62.2	1	-15	H			
721	70.3	70.1	5	- 1	H			
930	75.4		10	+13	H			

TABLE 8. Thermal Conductivity of FM 5072 VCK Carbon Cloth, USP95 Phenolic, Molded at 1,000 psi.

Temp., °C	K x 10^{-4} cal / cm sec °C		Error ± %	Mismatch %	STD	Specimen no.	Weight loss %	Comments
	Exp	Corrected						
0° Orientation, Virgin								
104	51.9	47.7	2	-41	H	4J	8.9	
207	60.1	55.5	1	-38	H			
321	64.4	61.8	3	-20	H			
320	65.0	62.4	4	-20	H			
406	65.2	62.5	1	-20	H			
503	60.6	58.2	0	-20	H			
705	66.5	65.6	5	- 7	H			
901	68.5		16	+1/2	H			
103	50.6	46.4	1	-41	H	4P	18.6	
204	59.8	56.4	1	-28	H			
310	62.1	58.2	4	-23	H			
310	60.7	57.7	1	-24	H			
519	54.1	51.0	1	-28	H			
695	55.7	53.2	3	-22	H			
868	57.8	56.0	1	-16	H			
90° Orientation, Virgin								
88	28.2	27.8	4	- 8	G	4F	6.2	
204	29.2	28.4	6	-13	G			
302	32.3	31.6	6	-10	G			
389	30.3	29.0	7	-22	G			
96	27.5	26.9	4	-11	G	4L	1.8	
190	29.7	29.1	3	-10	G			
303	32.5	31.9	4	- 9	G			
0° Orientation, Charred at 1500°F								
106	65.5	62.3	1	-24	H	4C	8.2	
308	80.1	80.0	4	-1/2	H			
511	88.3		3	+17	H			
704	87.4		4	+23	H			
897	89.6		8	+33	H			
705	87.1		4	+23	H			Decreasing temperature
711	80.3		22	+13	H			Decreasing temperature & vacuum
519	79.6		0	+ 6	H			Decreasing temperature
521	72.3	71.7	14	- 4	H			Decreasing temperature & vacuum
305	70.5	68.7	1	-13	H			Decreasing temperature
300	65.6	63.0	3	-19	H			Decreasing temperature & vacuum
118	54.7	50.8	1	-36	H			Decreasing temperature
109	55.2	51.2	1	-36	H			Decreasing temperature & vacuum
104	62.1	58.6	4	-28	H	4D	20.5	Oxygen in system*
103	58.7	54.9	1	-32	H			Vacuum
302	77.0	76.2	2	- 5	H			
496	87.2		2	+15	H			
686	92.9		1	+30	H			
894	93.5		5	+37	H			
716	88.5		1	+24	H			Decreasing temperature

*Applies to all runs on Specimen 4D.

TABLE 9. Thermal Conductivity of FM 5064 Charred Ablative Chamber Specimens and 7740 Pyrex Glass.

Temp., °C	K x 10^{-4} cal / cm sec °C		Error ± %	Mismatch %	STD	Specimen no.	Weight loss %	Comments
	Exp	Corrected						
30° Oriented FM 5064 Ablative Chamber, Charred at 6300°F								
96	68.0	65.2	3	-21	H	A	23.6	Density = 1.15 g/cc, two piece construction two ends not smooth*
307	87.0		4	+ 8	H			
509	90.6		3	+20	H			
737	94.5		1	+34	H			
925	93.5		6	+39	H			
918	94.6		2	-37	C			
1107	79.3		8	-42	C			Too low, disregard
92	84.6	84.3	4	- 2	H	B	7.4	Density = 1.16 g/cc, all ends smooth, mold psi 3000**
296	90.5		5	+12	H			
509	109		1	+44	H			
723	107		1	+51	H			
906	110		4	+63	H			
954	114		4	-23	C			
1118	123		6	-11	C			
Pyrex 7740 Glass								
132	33.3	33.6	7	+ 5	G			
252	35.5	35.7	6	+ 3	G			
369	38.5	38.6	7	+ 2	G			
252	36.1	36.4	11	+ 4	G			
138	31.7		10	+ 1	G			
138	32.3		8	+ 1	G			
252	35.1	35.2	8	+ 2	G			
104	32.6	32.9	8	+ 5	G			
113	37.6	33.4	3	-56	H			Tc#5, -1.6°C off.
221	39.9	35.8	3	-52	H			Tc#5, -1.9°C off.
320	43.0	39.1	1	-46	H			Tc#3, +1.1°C off.
408	47.8	44.4	1	-39	H			

*Applies to all runs on Specimen A.

**Applies to all runs on Specimen B.

calculated by adding 20 percent of the mismatch percentage to the experimental value. This correction factor was used only on those values which were lower than the conductivity of Pyroceram 9606 standard (STD H).

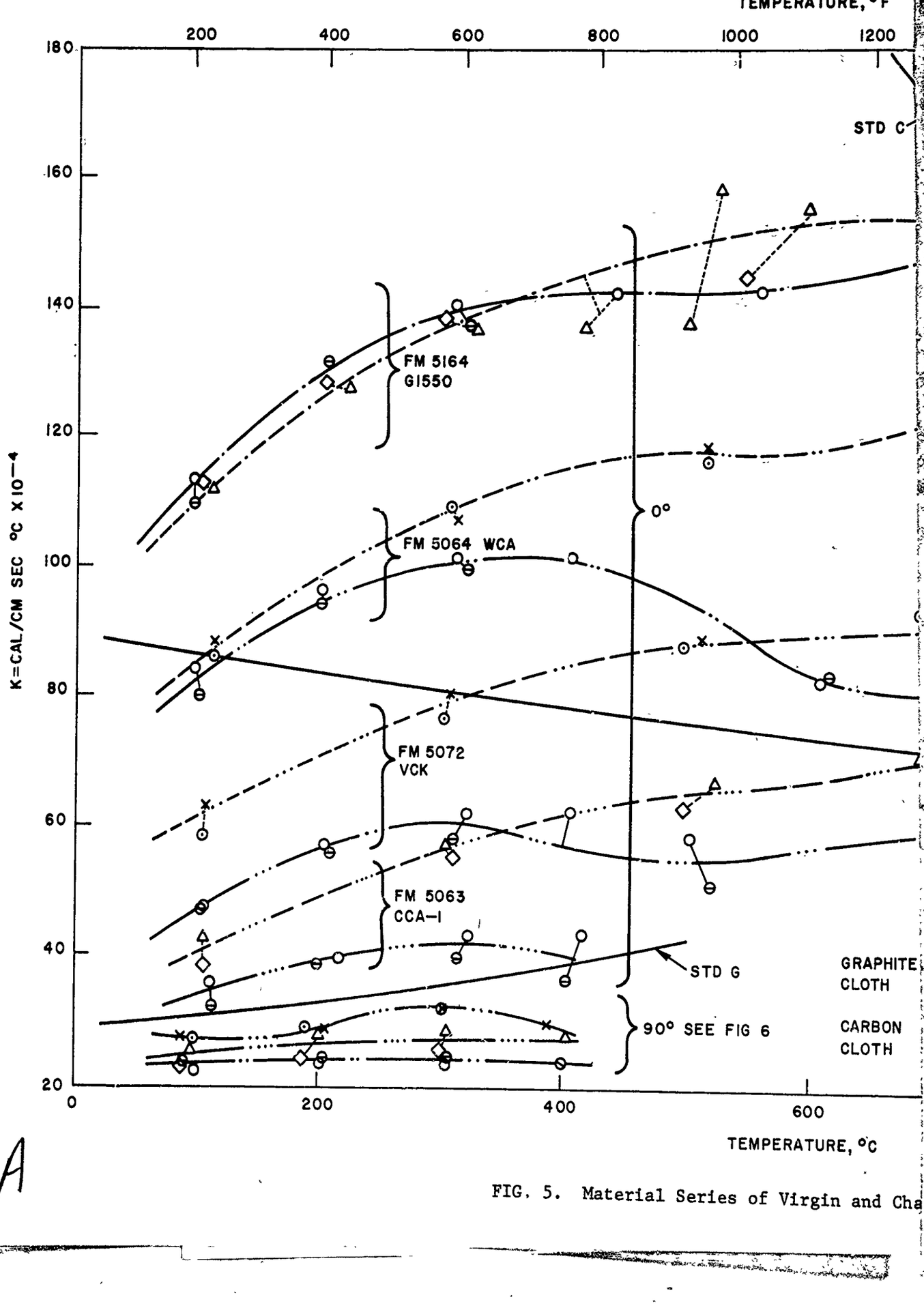
The percent error is not the absolute error and was reported because it is a measure of how well the heat flow through the cut-bar column had stabilized. It represents the difference in thermal conductivity of the specimen as compared to the top versus bottom standard. This error occurs because the temperature drop (ΔT) between TCs of each of the two standards is different and the greater this difference the greater is the error. Thus a small error assures one of a good K value except for the mismatch.

The percentage mismatch, between the K values of the specimen and standard at temperature, is given because it should be ±10 percent or less to obtain values within ±5 percent of absolute error as specified by the manufacturer of the apparatus. Unfortunately no standards are available between standards G (7740 Pyrex Glass) and H (Pyroceram 9606) or H and C (Alumina) so that specimens falling between these standards have a mismatch much greater than ±10 percent.

The specimen number is the panel number suffixed with a letter (e.g., specimen 2K was made from panel 2). The weight loss of each specimen during conductivity measurements is given; however, no allowance was made for absorbed moisture. Correlation of weight loss versus time or temperature was not determined because the time varied between 1 day and 1 week. Also, weight loss was affected by oxygen in the system which could not be completely eliminated by the argon purge because the apparatus was not absolutely vacuum tight.

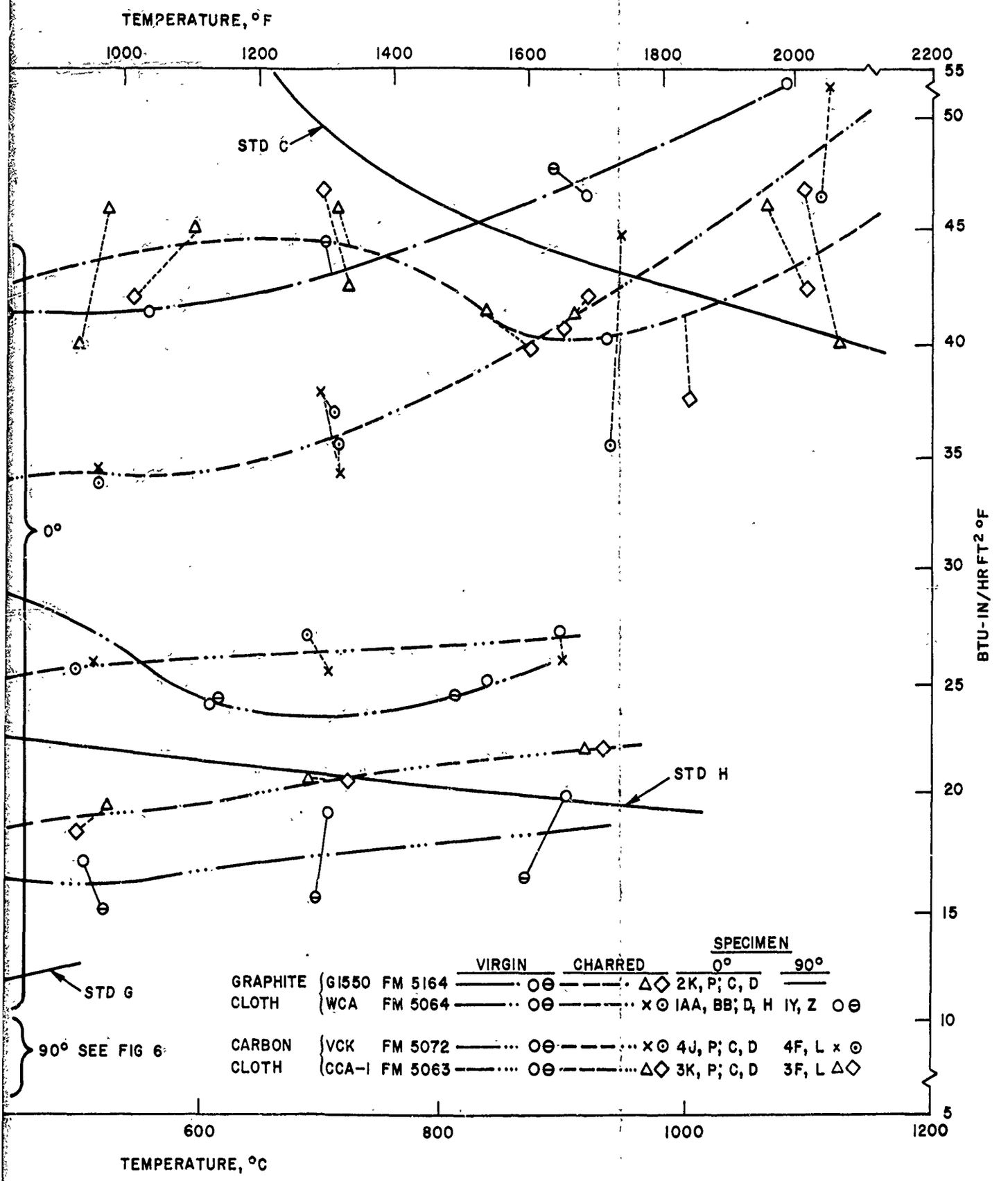
The comments column points out oddities which may affect thermal conductivity. Sometimes readings were taken before temperatures were fully stabilized to avoid maintaining specimen temperature high enough to continue charring over a weekend, or because the mismatch was so great that insufficient control existed in the guard heaters to achieve stable conditions. Comments like "TC 4, -1.7°C off" identifies a specific thermocouple (see Appendix) and indicates how far off it was from the ±1.0°C required.

Data from Tables 2 through 9 are graphically presented in Fig. 5 through 12 (corrected K values were used below the STD H curve). A typical legend established in Fig. 5 identifies the virgin and charred states as solid and dashed curves respectively; dots identify material type; symbols are listed in respective order of the specimen number (not repeated) and letter; a semicolon separates virgin from charred specimen letters. Thus for FM 5164 in Fig. 5, O is for 0° virgin specimen 2K, Θ is for virgin 2P, Δ is for charred 2C, and $\diamond$ is for charred 2D. Symbols and numbers for the 90° virgin specimens are listed together in respective order. Specimens were plotted individually and the curve drawn through the weighted average value to show the agreement between duplicate specimens. Curves



A

FIG. 5. Material Series of Virgin and Cha



terial Series of Virgin and Charred Specimens.

B

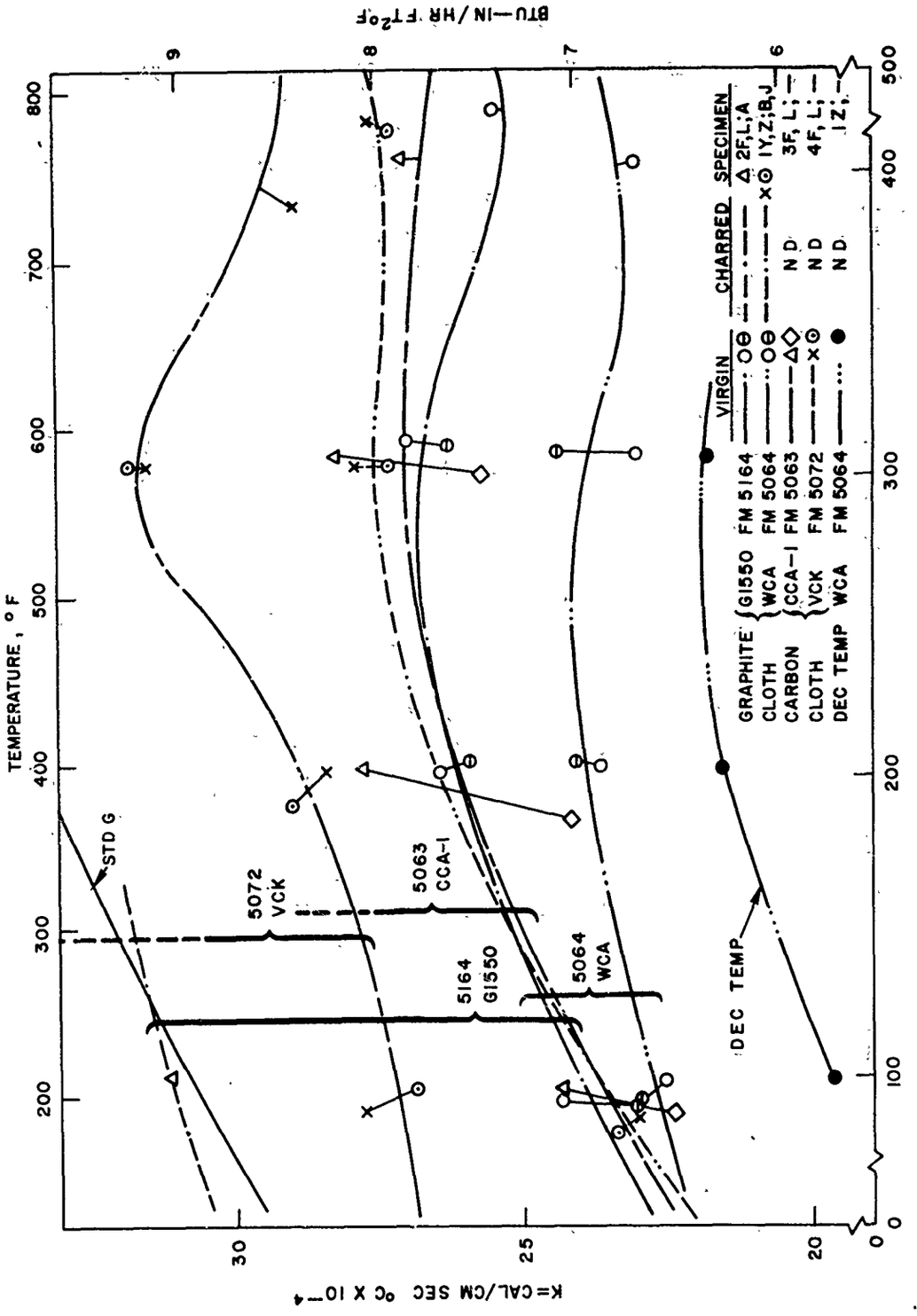


FIG. 6. Material Series at 90 Degrees.

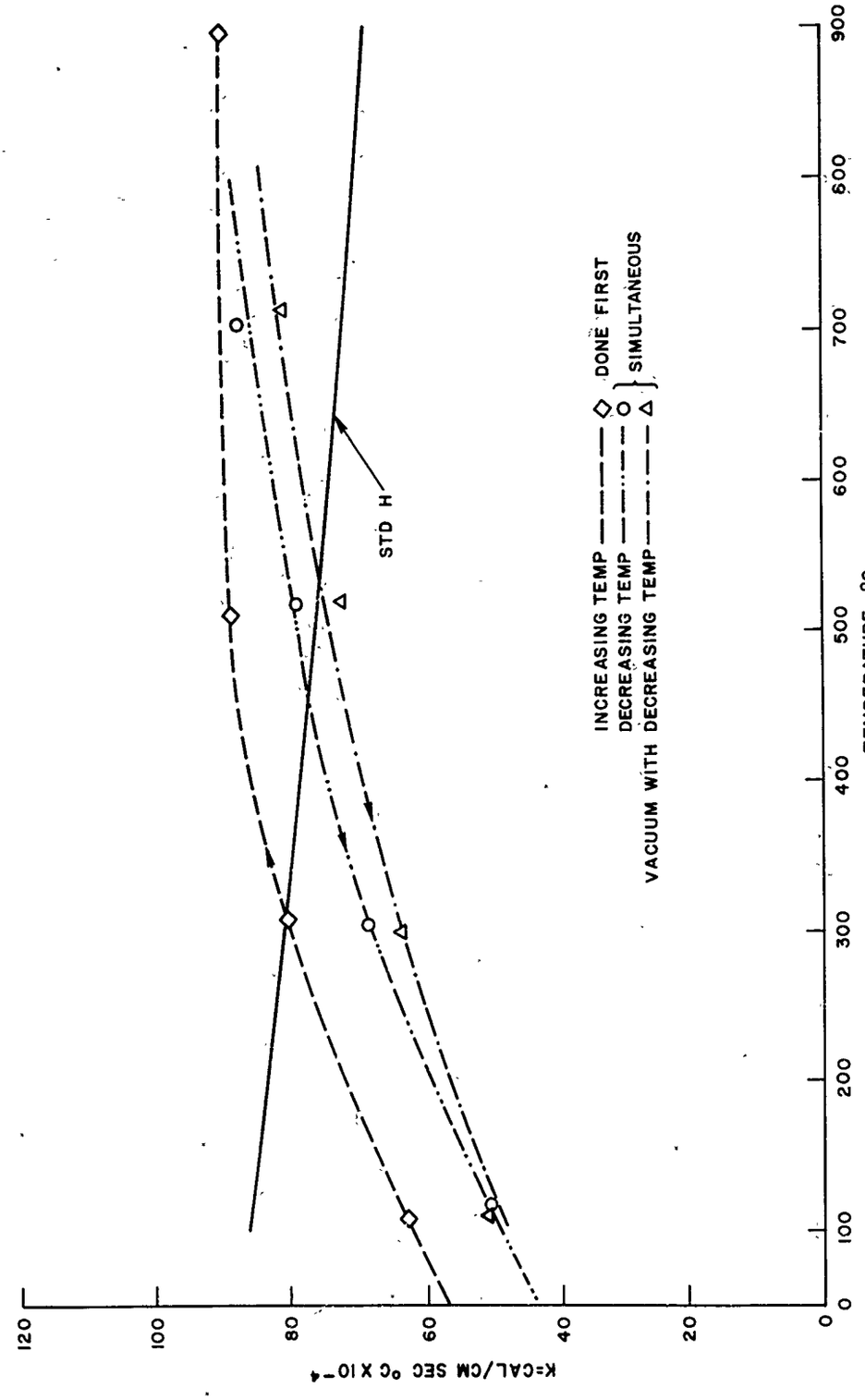


FIG. 7. Decreasing Temperature and Vacuum Effect on FM 5072 Charred 0 Degree Specimen 4C.

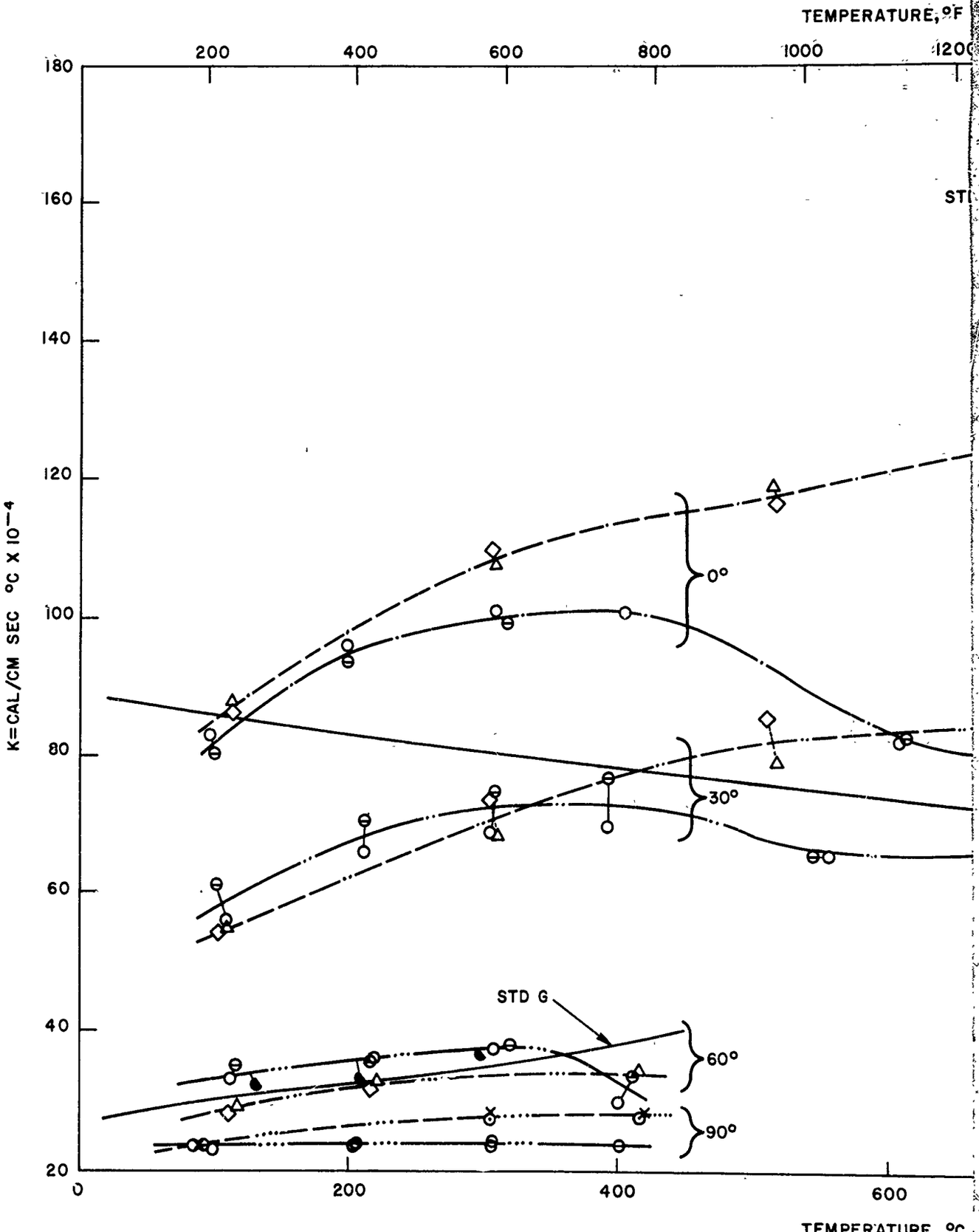
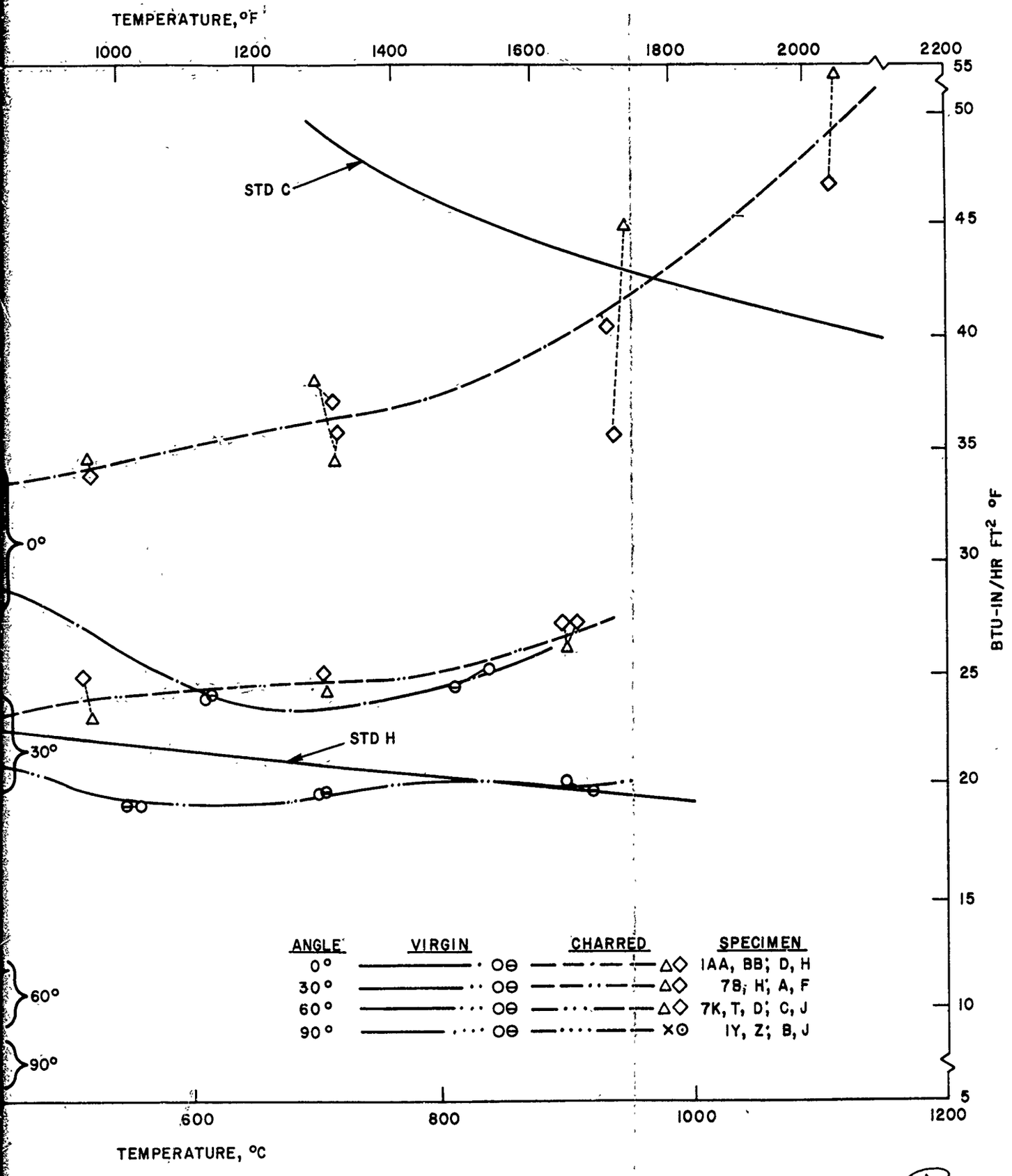
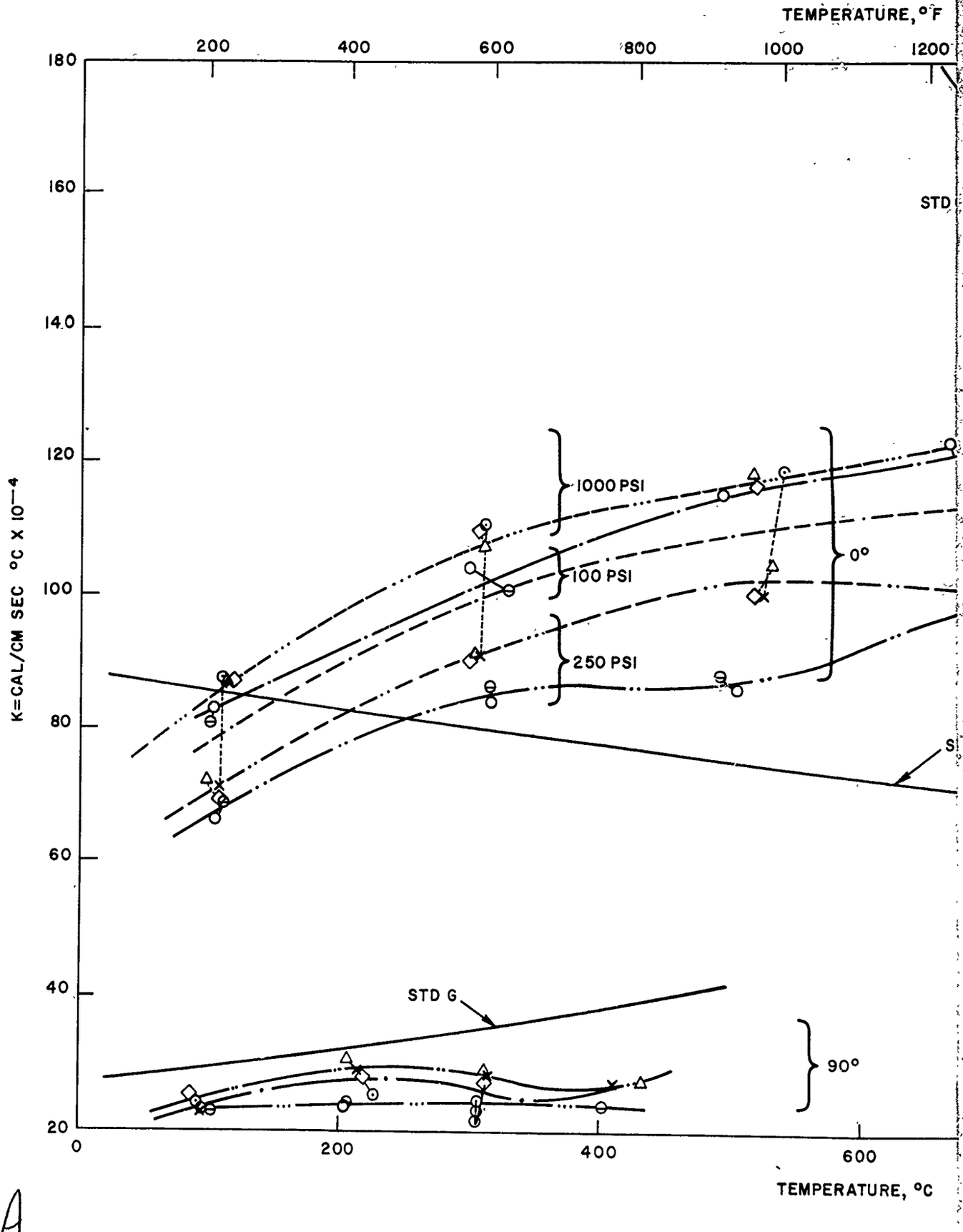


FIG. 8. Fiber Angle Series of

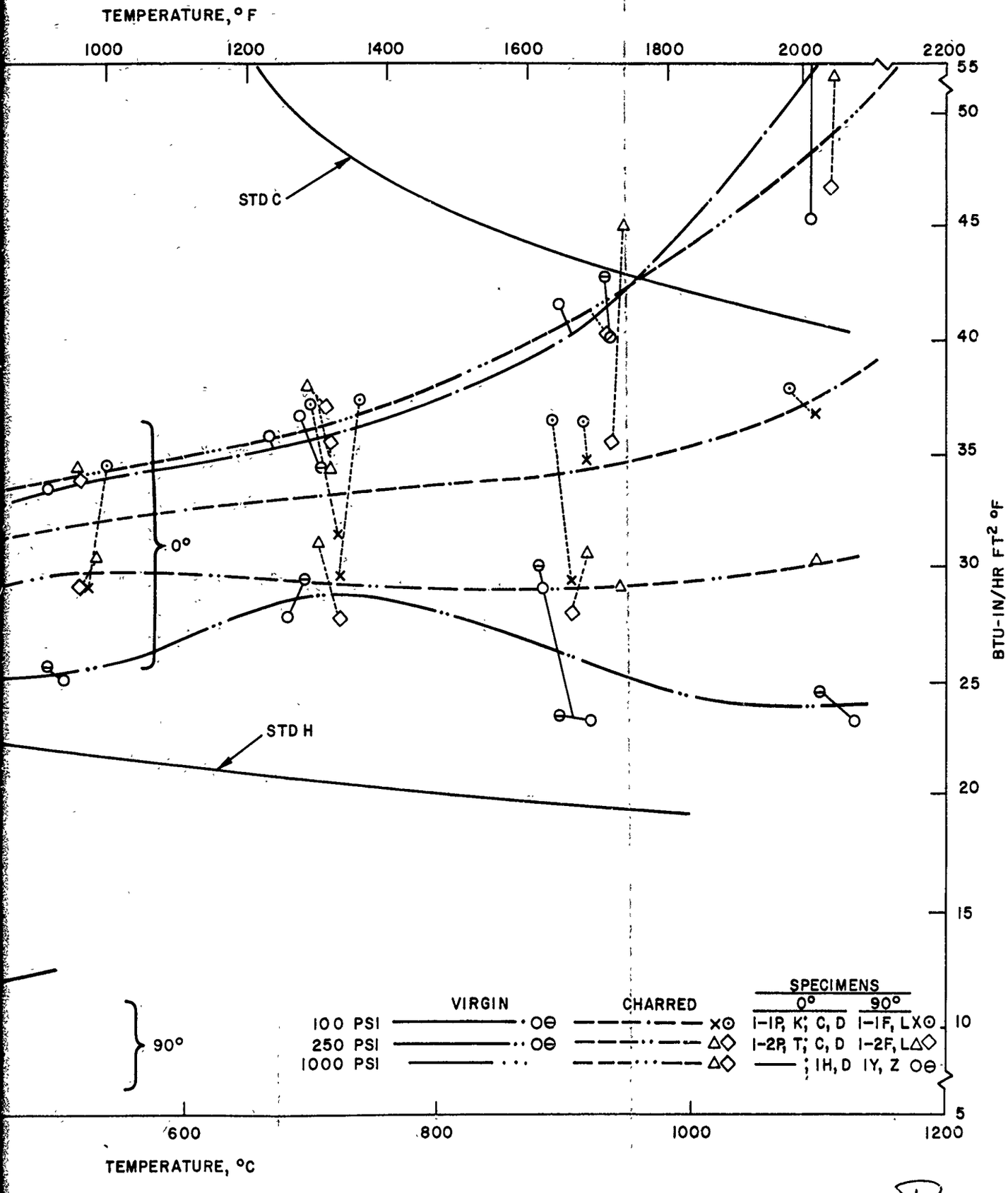


8. Fiber Angle Series of FM 5064.



A

FIG. 9. Molding Pressure Series



9. Molding Pressure Series of FM 5064.

B

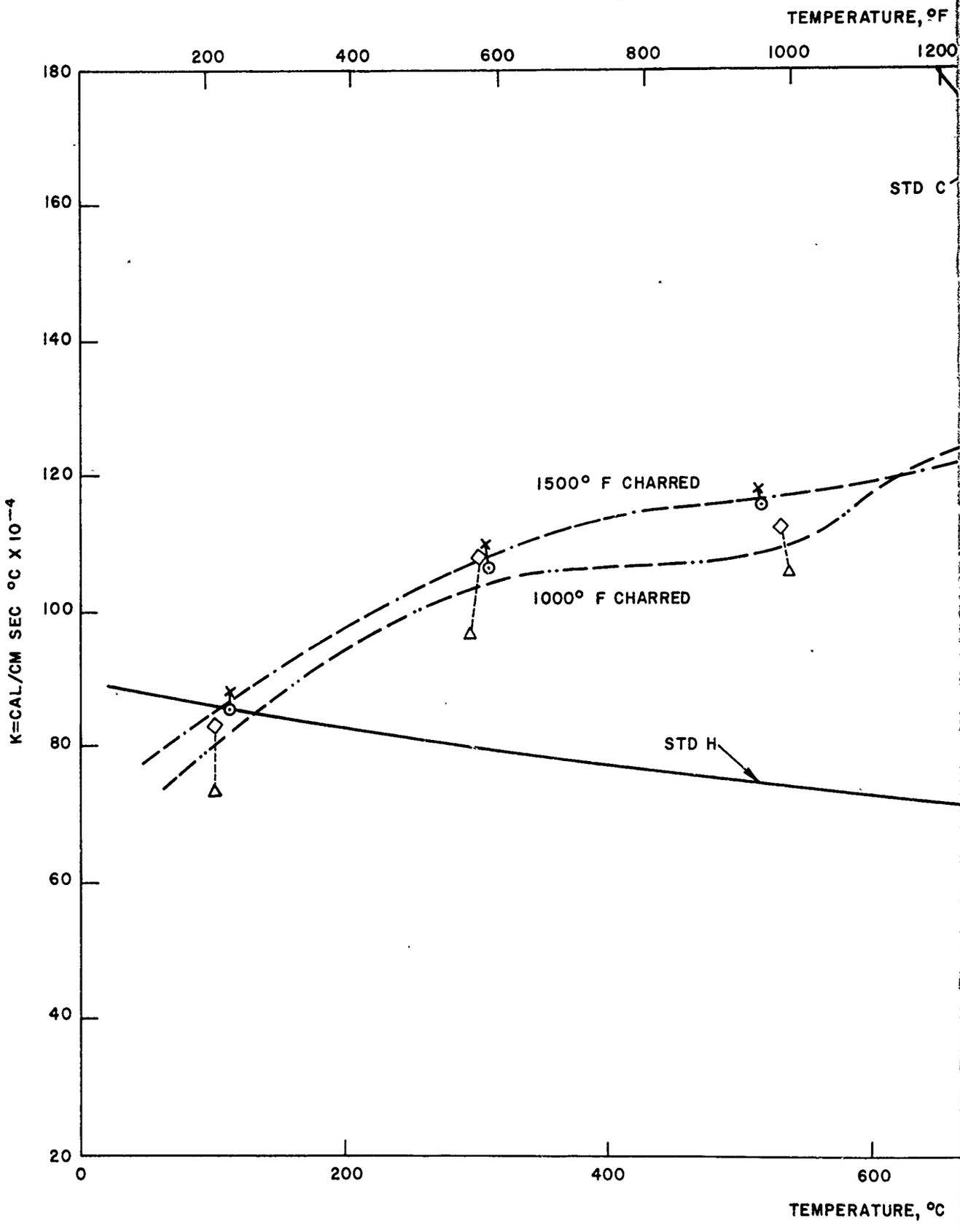
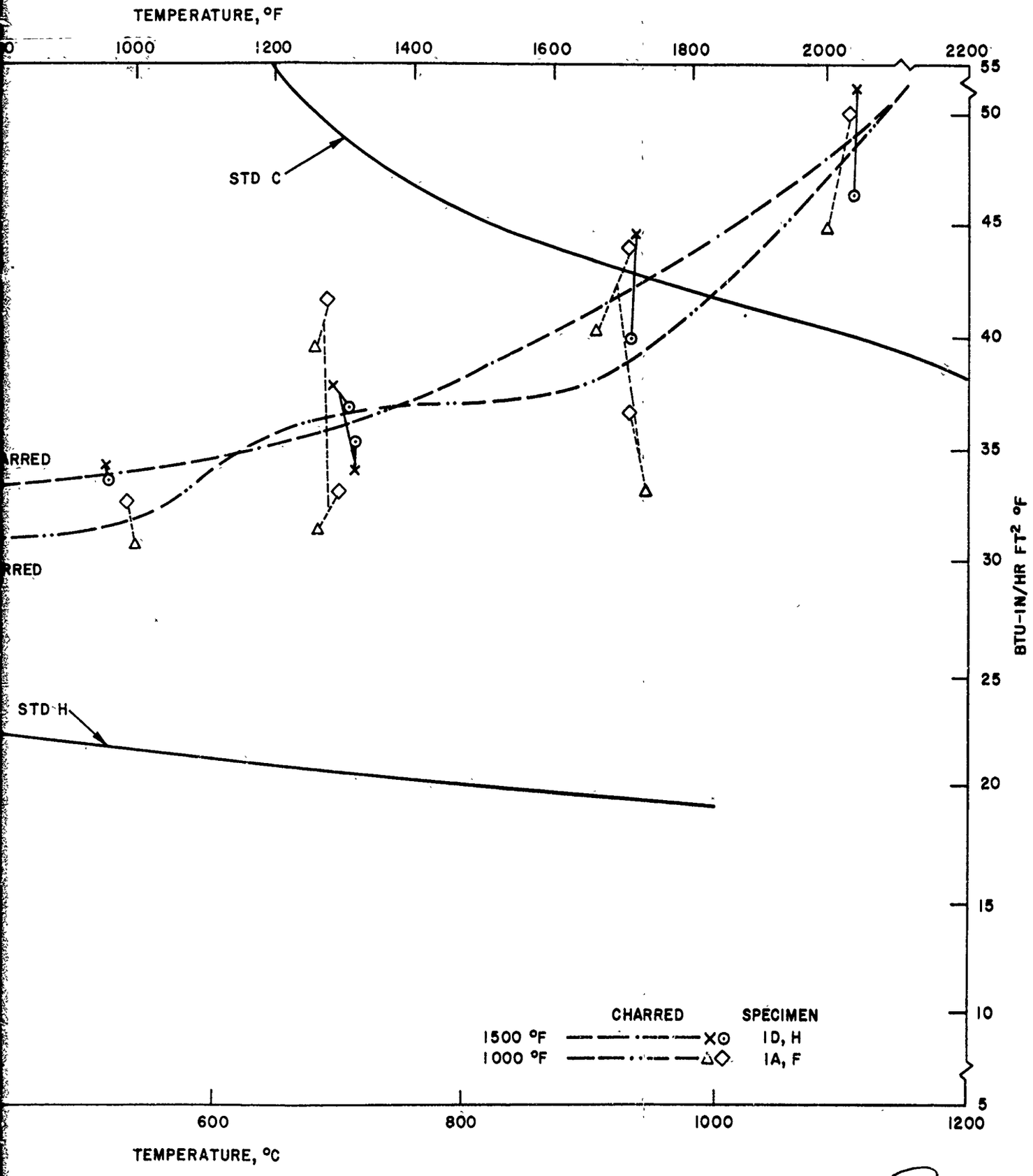


FIG. 10. Char Temperature Effect of FM 50



Temperature Effect of FM 5064 at 0 Degree Fiber Angle.

B 25

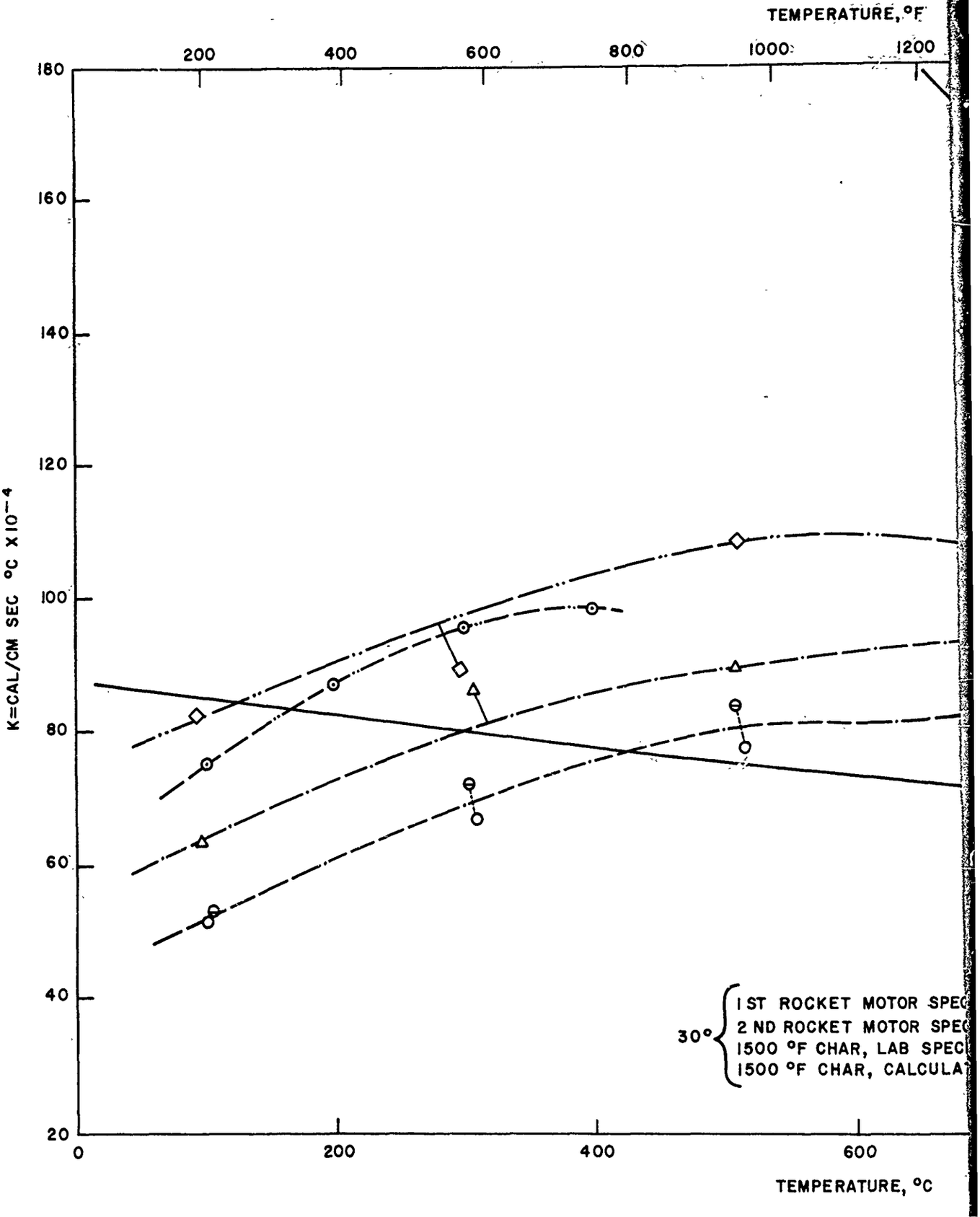
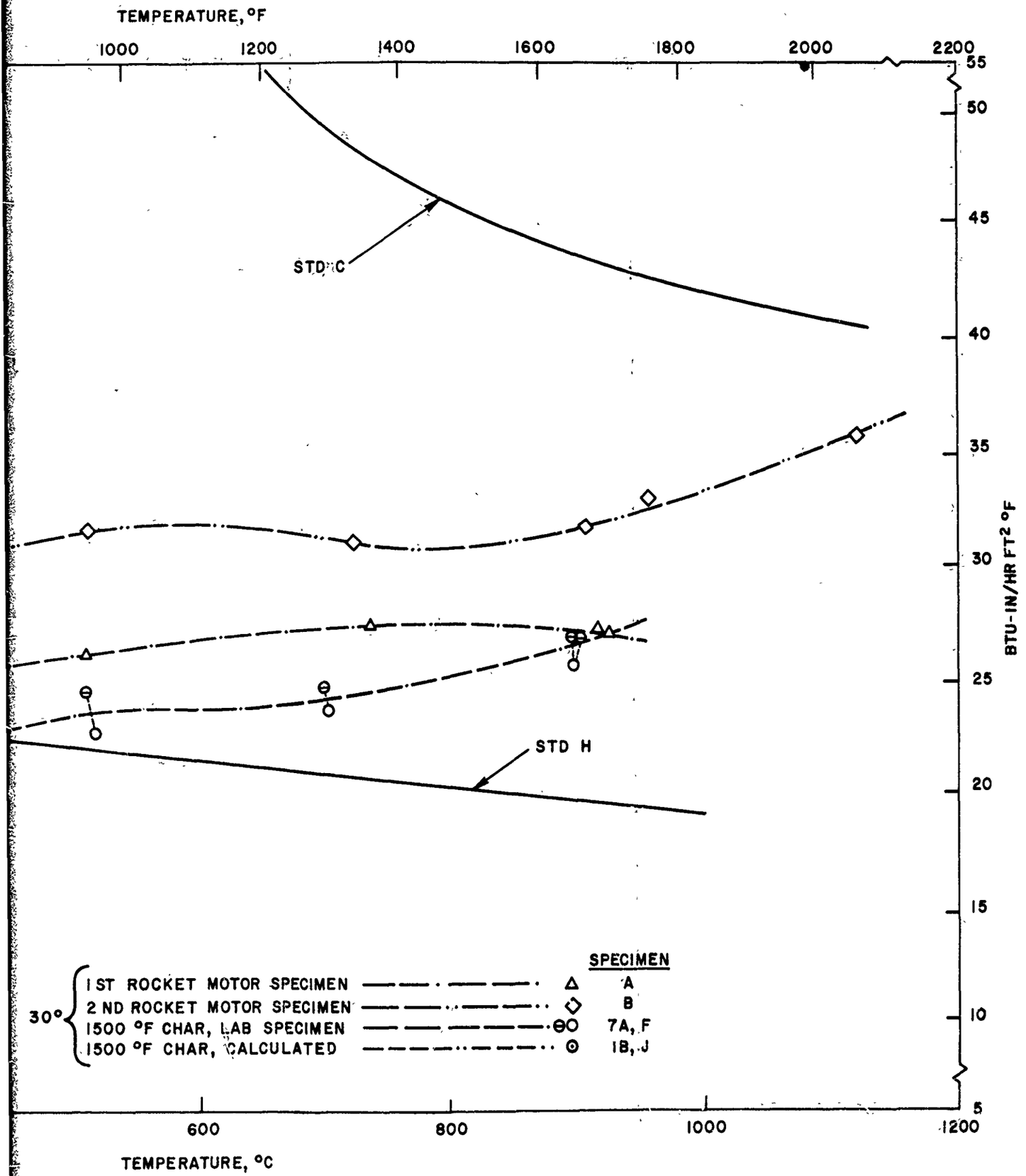


FIG. 11. Rocket Motor Fired Specimens Compa
Prepared Specimen.



t Motor Fired Specimens Compared with a Laboratory
en.

B

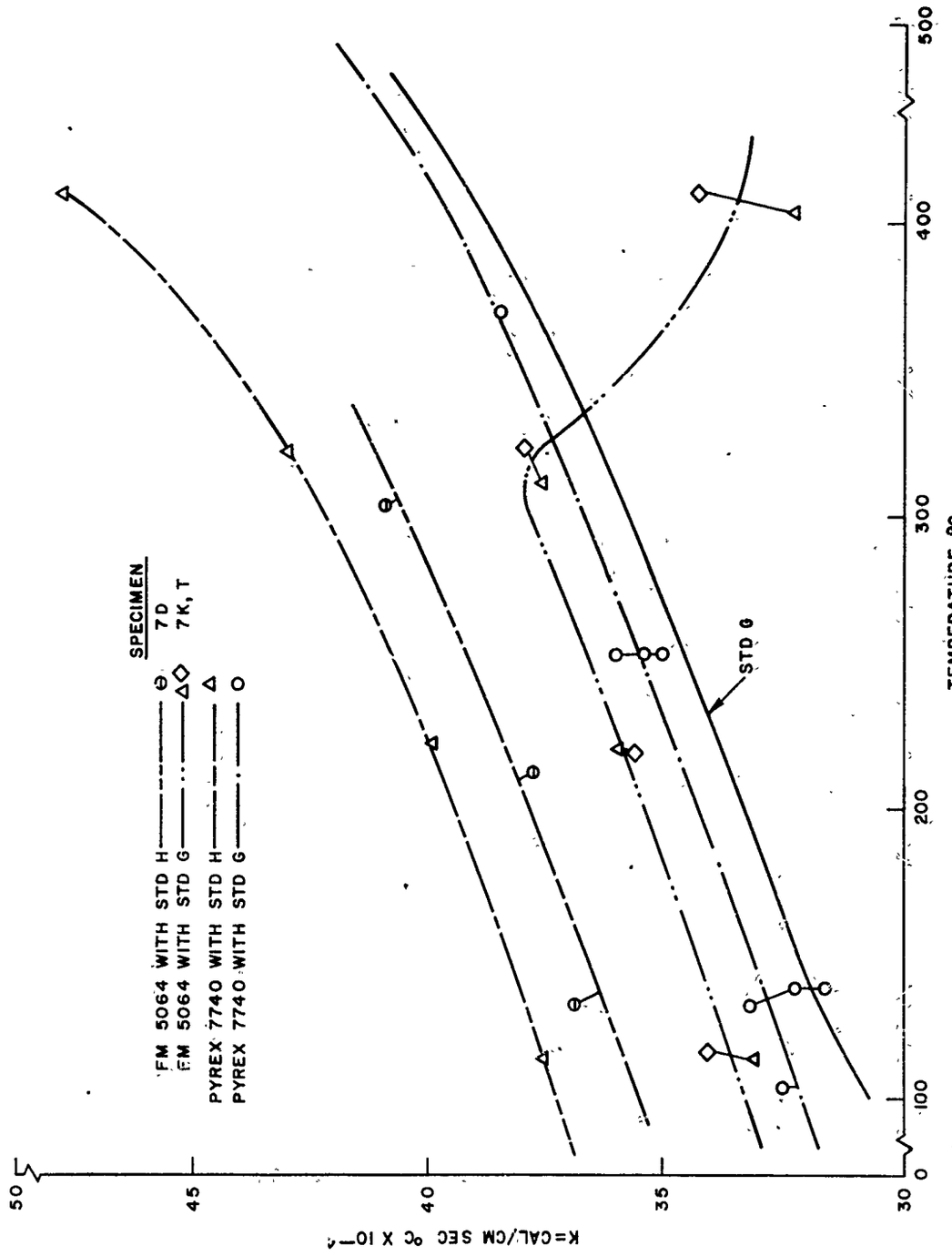


FIG. 12. Standard Mismatch Effect; Uncorrected K Values.

for each standard used were drawn (labeled solid line) because K values close to a standard curve are accurate whereas those values far removed from a standard curve are less accurate. Two standards were used on some specimens such as charred FM 5064 (0 degree) in Fig. 5 because its curve has a positive slope and crosses both the STD H and STD C curves. Both STD H and STD C were used at about 700°C for this specimen to show that the error due to mismatch was small.

A material series for charred and virgin specimens of four reinforcement cloth types are shown in Fig. 5 at 0 degree fiber orientation to indicate the magnitude of cloth-types-effect versus char and virgin effect. The 90 degree or across-ply specimens are plotted separately in Fig. 6 on an expanded scale.

Specimens were permanently changed in thermal conductivity after being heated above 400°C; therefore, they could not be rerun at a lower temperature to redetermine a questionable value. Because of this effect, all specimens were first tested at low temperature, progressing to the next higher temperature. Curves are shown in Fig. 7 for increasing temperature and decreasing temperature with concurrent K values under vacuum. The K values in Tables 2 through 9 are given in chronological order.

The effect of fiber orientation is shown in Fig. 8, the effect of laminate molding pressure in Fig. 9, and the effect of laboratory char temperature in Fig. 10.

A comparison of laboratory charred specimens (7A and 7F) with those taken from an ablative chamber is shown in Fig. 11. The ablative chamber specimens were taken from the wall of a rocket motor combustion chamber 2 and 3 inches downstream of the injector. Char thickness was only 0.70 to 0.75-inch thick so the first 0.500 inch of char at the hot wall was used. Two such pieces, 1-inch-diameter by 0.500-inch-thick, were stacked to make one specimen so that heat-flow was in the same direction as in the rocket motor. The motor internal diameter was 4 inches. The motor was fired 46 seconds, at 750 psi chamber pressure using an interhalogen oxidizer with a mixed hydrazine fuel (Ref. 1, chamber 10). Surface temperature of the char was about 2930°C (5300°F) and at 0.500-inch-depth it was about 870°C (1600°F) at termination of firing. Thus the ablative chamber char had undergone a higher char temperature than the laboratory specimens.

The effect of standard mismatch is shown in Fig. 12. Standard G is grade 7740 pyrex glass[1] and so a specimen was made from the same material to check the accuracy of STD G. The STD G specimen was also evaluated with standard H to determine the effect of specimen to standard mismatch. From these values a correction factor was calculated.

[1]Corning Glass Works Co., Corning, New York

COMPARATIVE ANALYSIS

MATERIAL SERIES

Two types of graphite cloth phenolic and two types of carbon cloth phenolic were evaluated. Laminates with graphite cloth have a higher thermal conductivity (K value) than those with carbon cloth. The type of reinforcing fiber has its greatest influence when heat is allowed to flow along the warp fibers axially as in the 0 degree oriented specimens in Fig. 5. When heat must flow across-ply, as for the 90 degree oriented specimens (Fig. 6), the fiber reinforcement type has little influence on the K value. This is true because graphite and carbon fibers have a relatively much higher thermal conductivity than does phenolic resin. Compare the following K values:

Along a graphite fiber[1]	2480 cal/cm sec °C x 10^{-4}
Along a carbon fiber[2]	537 cal/cm sec °C x 10^{-4}
Unfilled phenolic resin[3]	5.8 cal/cm sec °C x 10^{-4}

G1550 VERSUS WCA REINFORCEMENT

The highest conductivity was exhibited by FM 5164 with G1550 graphite cloth in the with-ply direction or 0 degree orientation. Factors contributing to the higher K value for G1550 versus WCA reinforced specimens are higher specimen density (panels 2 and 7, Table 1) and higher fiber density (Table 10). Factors detracting from this are the warp-to-fill fiber ratio, and to a lesser degree the resin content.

TABLE 10. Fiber and Fabric Properties Without Resin

Fabric[a]	Type	%C	Density g/cc[b]	M^2/g	Warp/fill	Ratio warp/fill	Weave[c]
G1550	Gr.	99.6	1.51	3	54/46	1.17	8HS
WCA	Gr.	99.9	1.42	3	27/21	1.28	Plain
VCK	C	99.0	1.47	6	40/36	1.11	5HS
CCA-1	C	97.0	1.85	80	52/47	1.10	8HS

[a]G1550, CCA-1 from HITCO; WCA, VCK from National Carbon Co.
[b]In Helium by vendor
[c]HS = harness satin

[1]National Carbon Co. Thornel 40
[2]VYB Yarn
[3]Ref. 4 and 5

CCA-1 VERSUS VCK REINFORCEMENT

The lowest conductivity, in the with-ply (0 degree) direction, is for FM 5063 with CCA-1 carbon cloth. Factors contributing to the lower K value of CCA-1 versus VCK reinforced specimens are fiber parameters of purity, and surface area, though the reverse should be true because of the specimen and fiber density.

GRAPHITE FABRIC VERSUS CARBON FABRIC

Graphite fabric reinforcement is more conductive than that of carbon, though the spread between the graphite and carbon fabric reinforced specimens for 0 degree orientation is not very great (Fig. 5). Graphite fibers have a higher conductivity, greater purity, less surface area, and greater warp-to-fill fiber ratio as seen in Table 10. The only factor detracting from this is specimen density, that is, the carbon reinforced specimens from panels 3 and 4 of Table 1 had a higher density (fiber packing) than did the graphite fiber reinforced specimens from panels 1 and 2.

CHAR VERSUS VIRGIN

Thermal conductivity of pre-charred specimens is almost always higher than that of virgin specimens. Both charred and virgin specimens increase in thermal conductivity as temperature increases. The slope of the curves for thermal conductivity is positive, (except for the dip due to charring).

Many virgin specimens start charring in the thermal conductivity apparatus at about 300°C with a consequent negative slope and dip in the curve. Partial recovery from the charring condition does not occur until about 700°C is reached, where the slope again becomes positive. This dip also occurs in charred specimens but at a higher temperature range, and is small between 300 and 700°C; it then becomes pronounced at 800°C with recovery at a higher temperature. The charred specimens undergo further charring or resin decomposition above the laboratory char temperature of 816°C (1500°F). This is apparent from the weight loss versus temperature curves seen in Fig. 13.

Absolute steady-state conditions were not attained, during the dip in the temperature range represented by the curve, even though guard heaters had been adjusted to steady-state conditions as indicated by monitoring thermocouples. The K values during the temperature dip are a false value because a true steady-state had not been attained in that dynamic resin, or coke decomposition was occurring. The dip in the curves is caused by charring or decomposition of the resin in the specimen. Phenolic resin decomposes slowly as temperature is increased above 300°C (Ref. 6) and is changed into a solid coke or carbon residue which is about 50 weight percent of the initial virgin resin. Heat energy

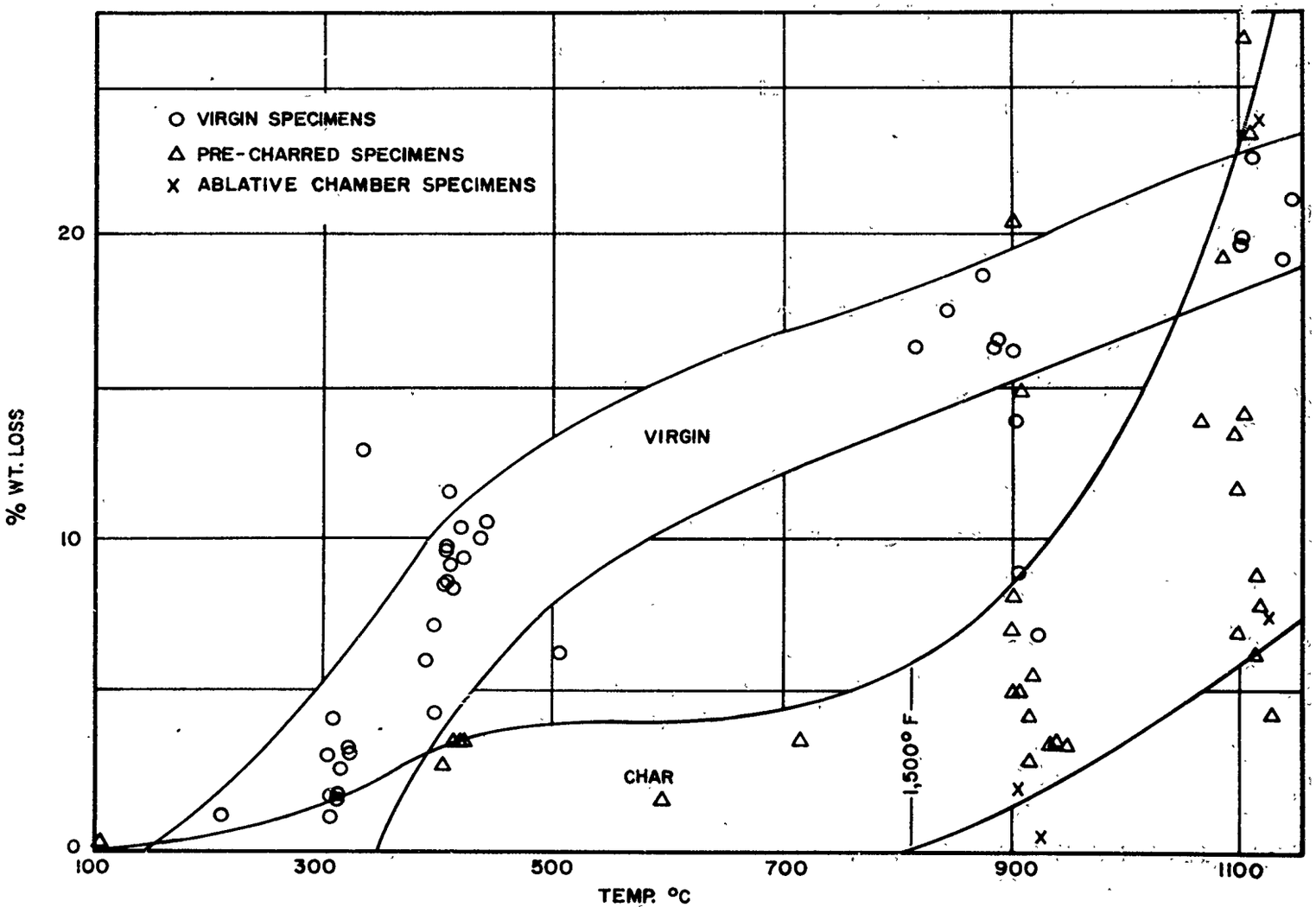


FIG. 13. Weight Loss of Specimens During Conductivity Measurements.

NWC TP 4647

absorbed by molecules in the resin is used to thermally crack or break the molecules into smaller constituents and is therefore unavailable for heat energy transport through the specimen. Further energy is absorbed as heat of vaporization in the formation of gases. Even further energy is absorbed as specific heat of the gases in raising their temperature. Most of this absorbed heat is then removed from the specimen as the expanded gases percolate through the charring matrix to a lower external pressure and are diffused into the zirconia insulation surrounding the specimen. In rocket motors, this process is known as ablative cooling (Ref. 1). Resin coke residue in pre-charred specimens undergoes further degradation because it is raised above its pre-char temperature of 816°C (1500°F) and is not completely degraded.

WITH-PLY (0 DEGREE) VERSUS ACROSS-PLY (90 DEGREES)

Across-ply conduction is much less than with-ply conduction. Across-ply conduction is controlled by parameters of the resin as much as by the fibrous reinforcement. The highest K values for virgin material across-ply are for FM 5072 VCK carbon cloth (specimens 4F and 4L) and the lowest are for FM 5064 WCA graphite cloth (specimens 1Y and 1Z). This is almost the reverse order of that found for the with-ply conduction for carbon versus graphite type reinforcement. This indicates that specimen density has a greater influence on K values in the across-ply direction than in the with-ply direction.

The primary factor contributing to the high K value for 90 degree VCK-reinforced specimens is specimen density. All factors for the VCK fiber in Table 10 contribute toward a high conductivity but probably to a lesser extent than laminate density.

CCA-1 (carbon) and G1550 (graphite) reinforced specimens have similar K values at 90 degrees orientation because the high conductivity of G1550 is offset by the relatively lower specimen density or fiber to fiber spacing. The K values at 90 degrees orientation for WCA reinforced specimens are lowest because these specimens had the lowest density.

VACUUM AND SPECIMEN DEGRADATION

The effect of vacuum on pre-charred specimens was to reduce the K value by about 5 1/2 percent. Specimen 4D (Table 8) was evaluated under vacuum before the specimen temperature was increased and gave a reduced value of 5 1/2 percent. Specimen 4C (Fig. 7 and Table 8) was evaluated under vacuum after decreasing temperature from 900°C; the effect of specimen degradation must also be subtracted and therefore decreased by 5 1/2 percent. The amount of gas available to transport heat across voids in porous specimens decreases in a vacuum (low pressure); virgin specimens are relatively non-porous and therefore not affected.

Resin or coke degradation during specimen evaluation depresses the K value of the laminate. Specimen 4C in Fig. 7 (Table 8) was degraded and its K value progressively depressed at successively higher temperatures, and to a lesser extent during successively lower temperatures due to the time factor plus the added specimen degradation caused by vacuum drawing off volatiles. At 300°C on the temperature decreasing curve, the specimen K value had decreased 13 1/2 percent from the value determined during temperature increase. At 900°C, the K value depression could not be determined because specimen degradation had occurred during temperature increase. Degradation of pre-charred specimens is low below their 816°C pre-char temperature and high above this temperature as measured by the weight loss curve of Fig. 13. Degradation of virgin specimens is greater and occurs at a lower temperature. The bottom curve in Fig. 6 shows the effect on specimen 1Z (FM 5064, Table 3) during a temperature decrease from 308°C.

FIBER ANGLE SERIES

The principal factor influencing thermal conductivity of laminates, herein investigated, is orientation of the fabric plane with respect to heat flow direction. It is clear from Fig. 8 that heat conduction is lowest at 90 degrees (across-ply) and highest for 0 degree (with-ply) and that the 30 and 60 degree specimens are intermediate.

An equation commonly used to calculate thermal conductivity for any fiber angle is:

$$K_\theta = K_{90} (1 + \alpha \cos \theta) \tag{1}$$

where:

K = thermal conductivity

θ = angle between fiber axis and heat flow direction

α = a constant for a given material or laminate

α is constant for a given material and is calculated from the known conductivities at 0 and 90 degrees orientation.

$$\alpha = \frac{K_0}{K_{90}} - 1 \tag{2}$$

For ablative chambers, the fiber angle θ is given with respect to motor center line rather than with respect to the chamber wall or heat flow direction so that the subscripts of K in Eq. (1) and (2) are reversed. Thus $K_\theta = K_0 (1 + \alpha \sin \theta)$ (Ref. 2). From the foregoing Eq. (2) it can be seen that if K_0 (with-ply K value) is four times as great as K_{90} (across-ply K value) that α is 3 and conductivity due to fiber angle varies (K calculated) as follows:

Angle, deg	K calc, %	K data, %	K 200°C
0	100	100	92.5 cal/cm sec °C x 10^{-4}
30	90	75	70 cal/cm sec °C x 10^{-4}
60	62.5	38	35 cal/cm sec °C x 10^{-4}
90	25	24	22 cal/cm sec °C x 10^{-4}

whereas FM 5064 at 200°C varied as shown under K data when expressed as a percentage. The curves for 30 and 60 degrees are lower than those obtained using Eq. (1). This discrepancy occurred because the specimen length to diameter ratio was too high. Heat flow through specimens with various fiber or lamina orientations are shown in Fig. 14. Heat flow can generally be maintained through the 0 or 90 degree specimens, rather than through external insulation, by properly adjusting the guard heater temperature. With the 30 and 60 degree specimens, the heat flow into the specimen from the insulation on one side and the out-flow from the specimen into the insulation on the other side cannot be circumferentially controlled. The K values for the 30 and 60 degree specimens are therefore 15 and 25 percent respectively too low in the above example according to Eq. (1). The effect can be reduced by turning half of the specimen 180 degrees as was done with the two piece specimens from the ablative chamber (Fig. 4 and 14). The effect can be reduced to insignificance by using an adequately low length to diameter ratio, such as is used in the guarded hot plate method (not verified by Ref. 5). The temperature (ΔT) across the specimen to specimen interface for the two piece construction was low and may be similar to that of unlike surfaces at the specimen-standard interface (Fig. 15).

Therefore, α could not be reliably determined for the 30 and 60 degree specimens to prove Eq. (1) for determining conductivity for any fiber angle orientation. However, α was readily determined from 0 and 90 degree specimens and found to increase in value as temperature was increased. Alpha for the material series is shown in Fig. 16 and is much higher for graphite fabric reinforced laminates than for carbon reinforced laminates. The slope of the line for graphite cloth reinforced specimens is constant for GI550, WCA, and the WCA in the molding pressure series in Fig. 17. Alpha, as used in computer programs for predicting heat flow and char depth in ablative chambers, is constant from 0 to 3100°C (Ref. 2) and is the same for virgin and charred materials. The data confirms the magnitude of values for α, but its constancy with increasing temperature is not confirmed. The great variation of α from GI550 to WCA reinforced laminates is due to the relative difference in K value of the 0 degree specimens.

MOLDING PRESSURE SERIES

Thermal conductivity curves of specimens molded at three different pressures are grouped in Fig. 9, with the 1,000 psi curve being highest, the 100 psi curves being medium, and the 250 psi curves being lowest for

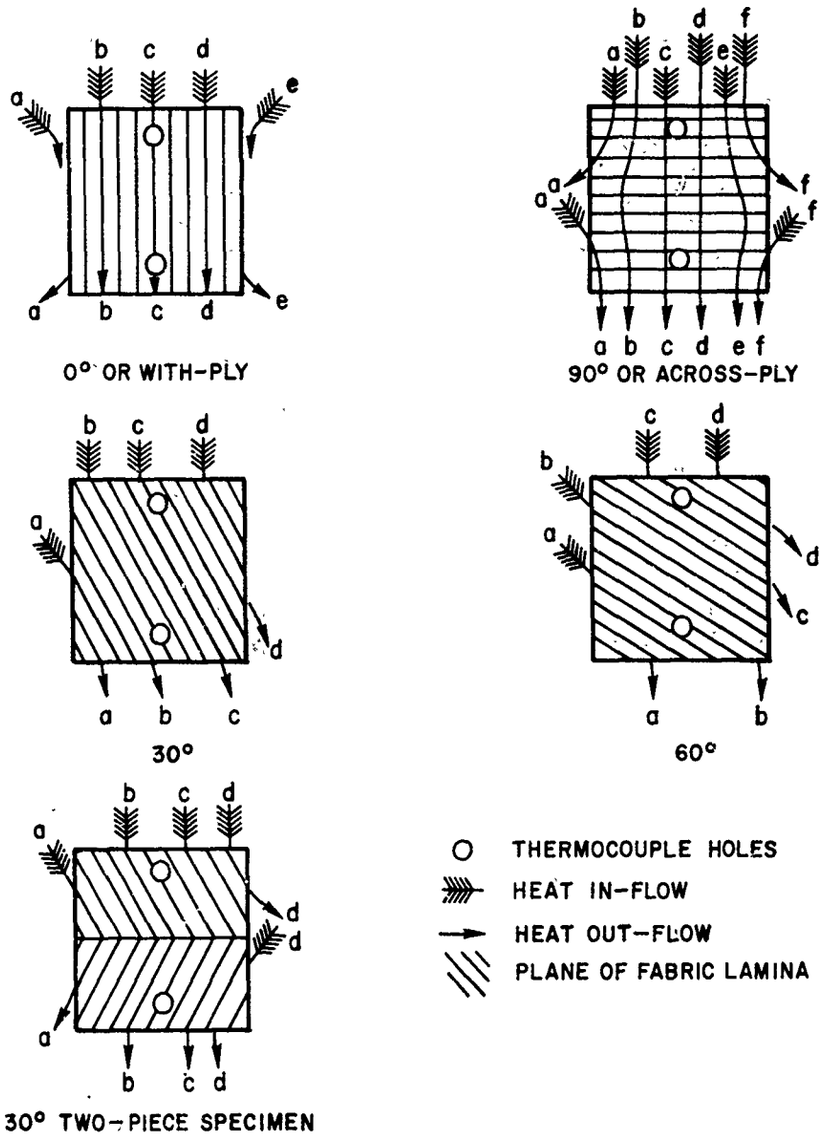


FIG. 14. Heat Flow in Specimens with Various Lamina Angles of Orientation.

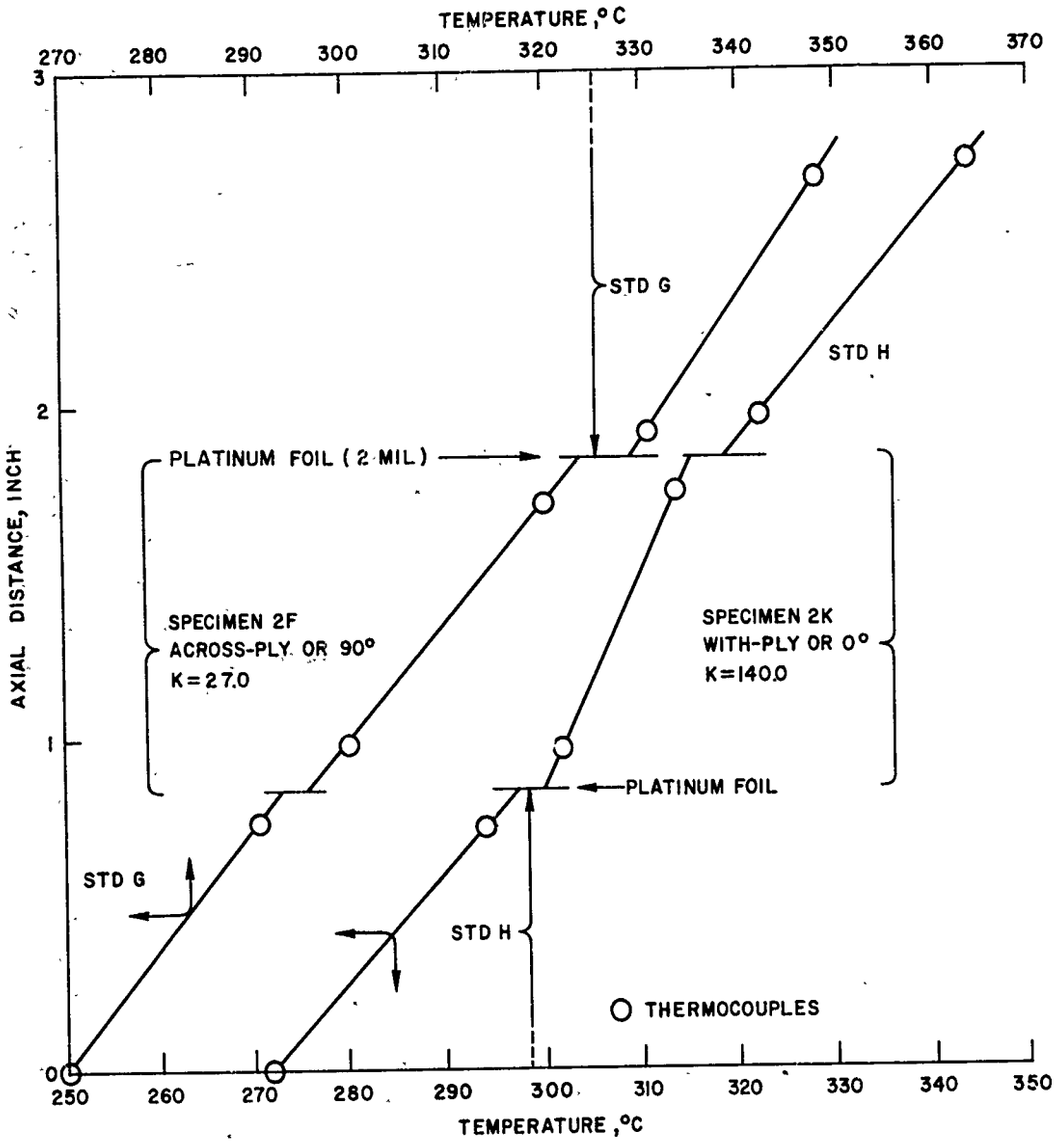


FIG. 15. Temperature Drop Across Two Standards and 0 and 90 Degree Specimens of FM 5164 Graphite Cloth Phenolic.

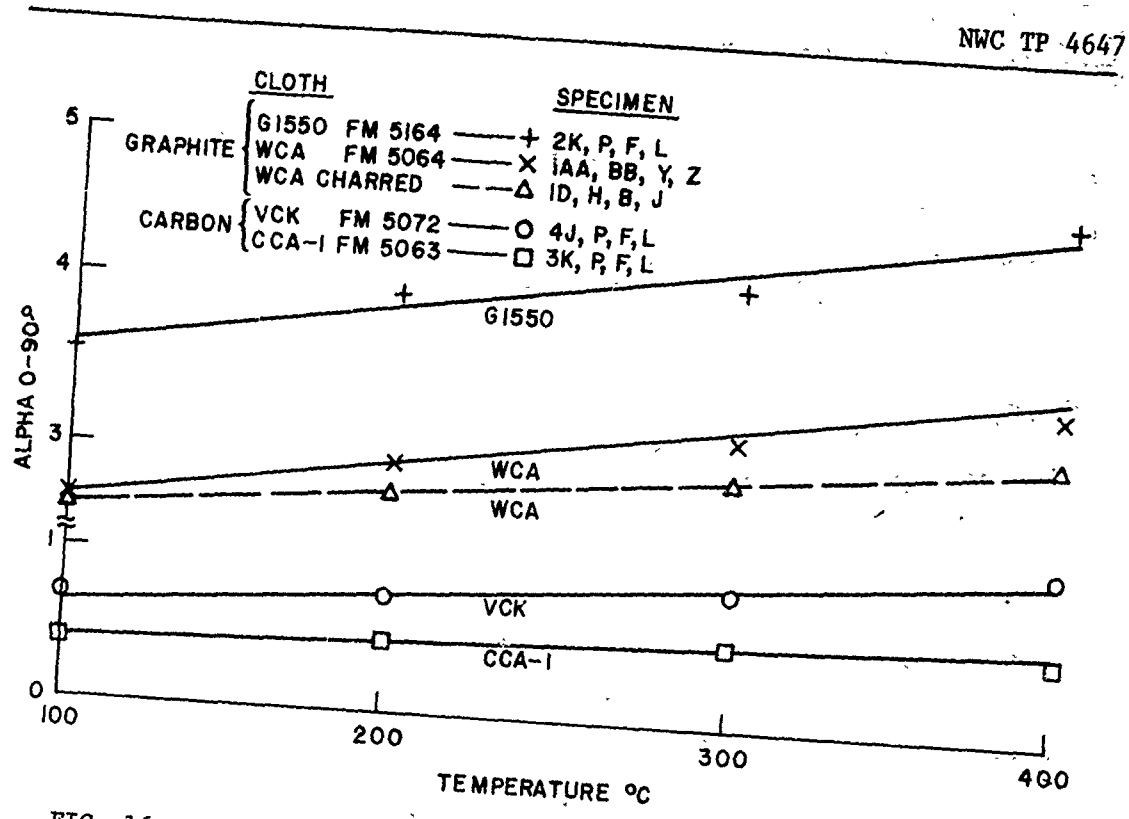


FIG. 16. Alpha for the Material Series of Phenolic Laminates.

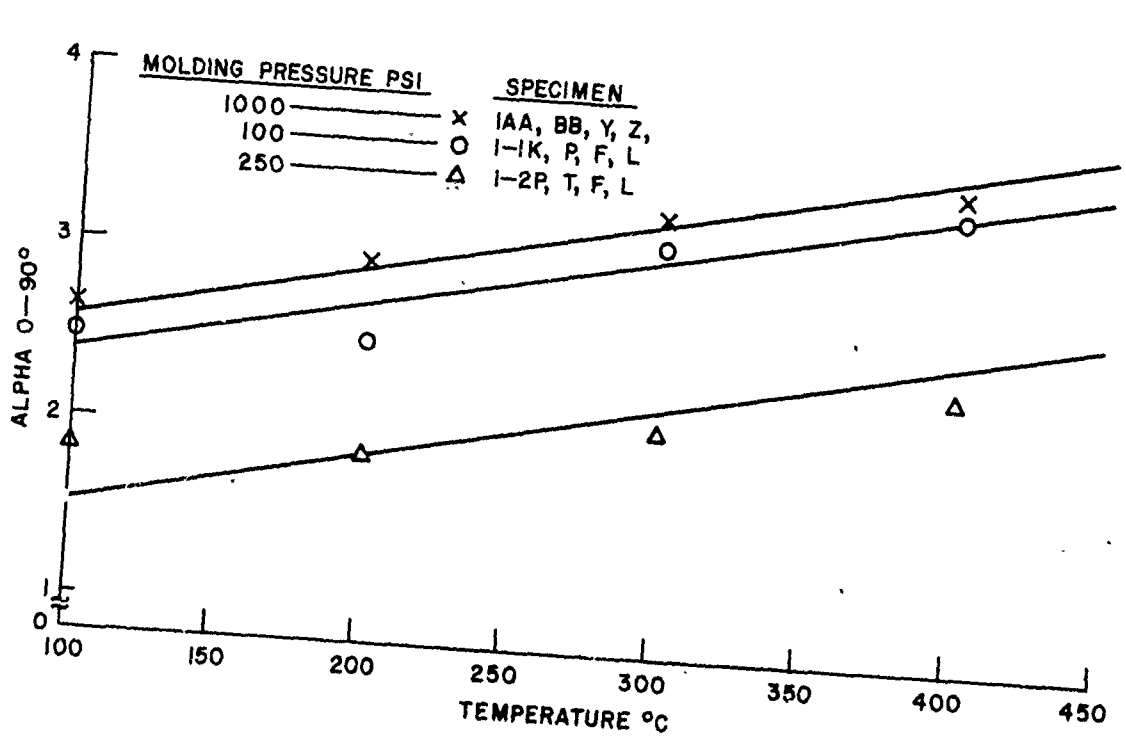


FIG. 17. Alpha for the Molding Pressure Series of Virgin FM 5064.

the 0 degree specimens. The 100 and 250 psi curves are reversed from that expected for molding pressure. That is, at a 100 psi molding pressure, less resin flow is expected resulting in a laminate with a lower density and higher resin content than for a 250 psi laminate. Therefore, a lower K value is expected because of the lower density and higher resin content (Ref. 4 and 5). The resin content (line e Table 1) is highest for 1,000 psi, medium for 100 psi, and lowest for the 250 psi as confirmed by weight loss and char density in Table 1. This may explain the medium position of the 100 psi specimens. The effect of resin content at 0 degree is so weak that the K values for the 1,000 and 250 psi curves are the reverse of what is expected from resin content. The degree of resin cure (inversely proportional to acetone extraction) correlates with the relative position of the 1,000, 100, and 250 psi curves. The effect of resin cure on K is not understood except that it may have contributed to the dip in the curve for the virgin 250 psi molded specimens.

K values for the across-ply (90 degrees) specimens are highest for 250 psi, medium for 100 psi, and lowest for the 1,000 psi specimens. Resin content has a greater effect on K values for across-ply specimens. The order of the curves is proper as expected from the average resin content.

CHAR TEMPERATURE EFFECT

Specimens charred at a higher temperature should have a greater portion of the phenolic resin degraded (approaching elemental carbon) and should therefore have a higher thermal conductivity. This was verified as seen in Fig. 10, but the effect is of a minor nature. Fiber orientation at 0 degree has a much greater influence on conductivity than the degree of resin degradation and masks the effect of char temperature. The only other difference between the 1000 and 1500°F char specimens is a 0.8 percent difference in weight loss during charring (Table 1); char density and other parameters are identical.

ABLATIVE CHAMBER SPECIMENS

Two specimens prepared from a fired ablative chamber (Ref. 1) were compared with the specimens charred in the laboratory as shown in Fig. 11. The higher laminate resin content and lower char density in the ablative chamber specimen (Table 1) tend toward a lower K value but this effect is offset by the use of a two-piece specimen construction shown in Fig. 4 and 14. The curve for specimens 7A and 7F is too low as discussed in the section on Fiber Angle Series. A truer curve for laboratory char for 30 degrees orientation was calculated using the equation $K_{30°} = K_{90°}$ $(1 + \alpha \cos 30 \text{ degrees})$ for specimens 1B and 1J and the values of α for charred WCA in Fig. 16. This curve for 1B and 1J is between the curves for ablative chamber specimens, and shows good correlation, especially since the ablative chamber curves may be slightly low because of the non-axial flow of heat in these two-piece specimens (Fig. 14).

CONFIDENCE LEVEL

The accuracy of thermal conductivity values is ±5% on those values which lie within ±10% of the curve for the standard, that is, where the specimen curve lies close to or crosses a standard curve. Values lying halfway between the STD H and STD C curves have the lowest confidence level and are of an unknown accuracy; however, these K values should differ less than ±20% from the true value. A correction factor was applied to the values below the curve for STD H to increase the confidence level; therefore, the K value should be within ±10% of the true value.

A correction factor which is 20% of the mismatch was determined as a compromise between the pyrex specimen and specimens 7K, T, and D (Fig. 12). The K value for the pyrex specimen evaluated at 113°C with STD H (Table 9) was corrected as follows:

$$37.6 + [\underbrace{20\%}_{\text{correction factor}} \underbrace{(-56\% \text{ mismatch})}_{} \underbrace{37.6}_{\text{K data}}] = \underbrace{33.4}_{\text{K corrected}} \frac{\text{cal}}{\text{cm sec °C}} \times 10^{-4}$$

The corrected K is still a little higher than 32.6 cal/cm sec °C x 10^{-4} obtained with STD G at 104°C, but is within 5 percent of the curve for corrected values. By the same process, specimen 7D in Fig. 12 was over corrected by about 10 percent near 100 and 200°C; however, since laminate specimens are subject to greater variation than a pyrex specimen, the correction factor was judged adequate though not absolutely accurate. Similar correction factors could have been found using Pyroceram and Alumina specimens for correction of values between the curves of STD H and STD C. These factors were omitted because of cost, time and the dubious accuracy of this technique. The inventor[1] of the 3M thermal conductivity apparatus has developed a method of correcting for large mismatches between specimen and standards. His technique was not available for this program and requires the installation of more thermocouples and a computer program to reduce the data. One such method is described in Ref. 7.

A correction factor was found to be of little importance for K values between the curves for STD H and C. Many data points falling in this range were obtained using both STD H and C on the same specimen at nearly the same temperature. Some of these values correspond satisfactorily using either STD H or C. Other values disagree radically but about half of the disagreements are in the wrong direction. That is, a correction factor would render about half of these points better and half worse by an equal amount. Thus plotting experimental K values above the curve for STD H gave the best results when no correction factor was applied.

[1]Dr. Parvis Mahmoodi, 3M Company, St. Paul, Minn.

The uncertainty of contact resistance at the specimen to standard interface was not investigated. Contact resistance varies due to surface smoothness, flatness, and pressure. The latter changed an unknown amount due to thermal expansion and shrinkage during charring. The magnitude of contact resistance may be estimated for two specimens from the curves in Fig. 15. The degree of uncertainty in the K values is low because the ΔT across the specimens is small. ΔT increased with temperature and fiber angle for specimens in Fig. 15 as follows:

Specimen 2F at 90°		Specimen 2K at 0°	
°C	ΔT °C	°C	ΔT °C
92	6.7	93	6.5
311	21.0	308	12.0
420	35.0	1120	24.0

K values for specimen 1-1F and 1-1L are 15 to 20 percent lower than those reported by C. D. Pears, et al (Ref. 4) for across-ply direction. Specimens 1AA and 1BB are 38 to 45 percent lower than the with-ply values in Ref. 5. These variations are chiefly due to differences in graphite cloth type, resin content and laminate density, and variations are in the expected direction. Specimens of FM 5064 were evaluated in the across-ply and with-ply direction in Ref. 8 but this laminate had a higher resin content and higher specific gravity, though the graphite cloth type was the same.

Weight loss of specimens subjected to a varied time-temperature environment during evaluation of K was significant and affected the value of K considerably. Thus the confidence of obtaining repeatable values is low. No correlation could be established for weight loss versus thermal conductivity.

PHOTOMICROGRAPHS

Selected specimens were vacuum impregnated with epoxy, sanded, polished, and photographed.

A virgin graphite cloth phenolic laminate is shown in Fig. 18. The fabric is oriented in a plane perpendicular to the plane of the page so that warp fibers are seen end-on and fill fibers are seen in side view. The light grey speckled ovals are the warp fiber bundles (thread or yarn) and the sinuous strips are the fill fiber bundles. The uniform grey and black areas between are resin. The same laminate is shown in Fig. 19 with the plane of the fabric in the plane of the page. The filaments (white) are seen in a side view as the warp fiber bundles weave over and under the fill bundles at 90 degrees. Note the presence of microcracks and pores (black) in the resin (grey).

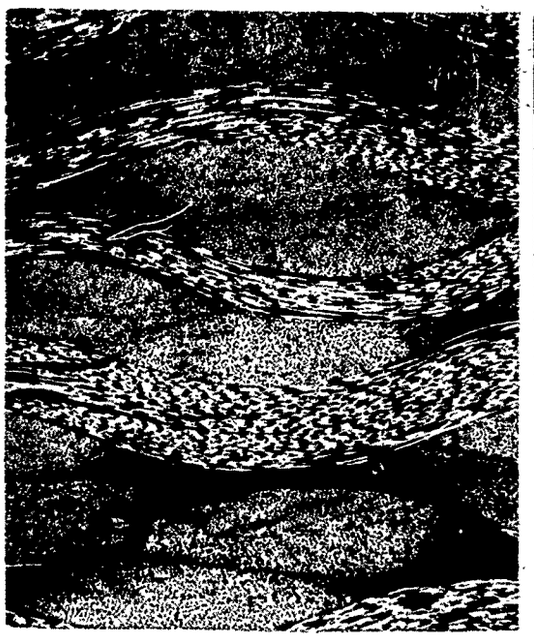


FIG. 18. FM 5064 Laminate of 0 Degree Specimen 1BB (50X).

FIG. 19. FM 5064 Laminate of 90 Degree Specimen 1Y (50X).

Individual filaments of graphite fibers (1/2 mil diameter) in a fiber bundle are seen end-on and in side view (bottom) in Fig. 20. Each filament acts as a high conductivity channel. The resin (grey speckled area) between the fibers holds the fibers in place and is of low conductivity. The light specks in the resin are carbonaceous resin filler. The fibers are not round but are highly convoluted and have microporosity (not seen). The convolutions and microporosity interrupt the path of heat flow making the fibers less conductive than monolithic graphite. The VCK carbon fibers seen in Fig. 21 are very similar in appearance to graphite fibers. The laminate for VCK (panel 4 Table 1) in Fig. 21 has a higher density than that for WCA (panel 1) in Fig. 20. Consequently, the fibers are more closely packed in the high density panel as seen in Fig. 21. The irregular black spots are surface anomalies due to imperfect polish or cleanliness of the specimen surface.

A photomicrograph of laboratory charred specimens is shown in Fig. 22. The VCK fiber remains unchanged, but the resin matrix has been reduced to a black porous char (grey speckled area between fibers). The uniform dark grey areas are epoxy resin used to hold the fibers in place during polishing. Figure 23 shows a specimen which has changed from the virgin to the charred state during thermal conductivity evaluation in the thermal conductivity apparatus. The maximum temperature it reached is essentially the same as that shown in Fig. 22. Note the similarity of these two photomicrographs.

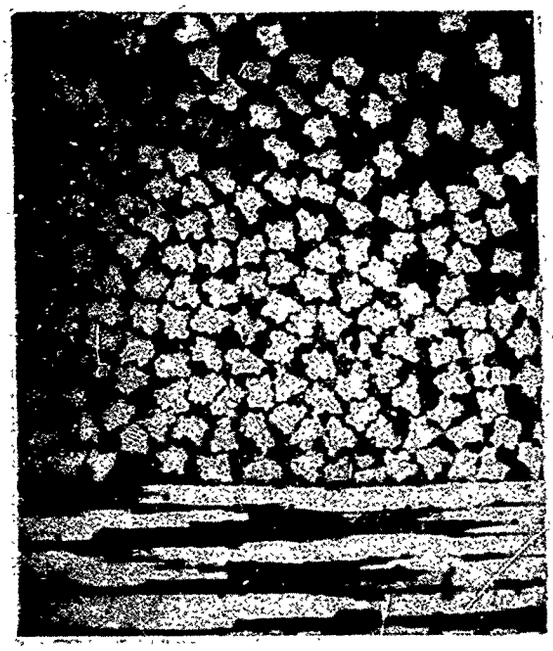


FIG. 20. WCA Fibers of Virgin Specimen 1BB (500X).

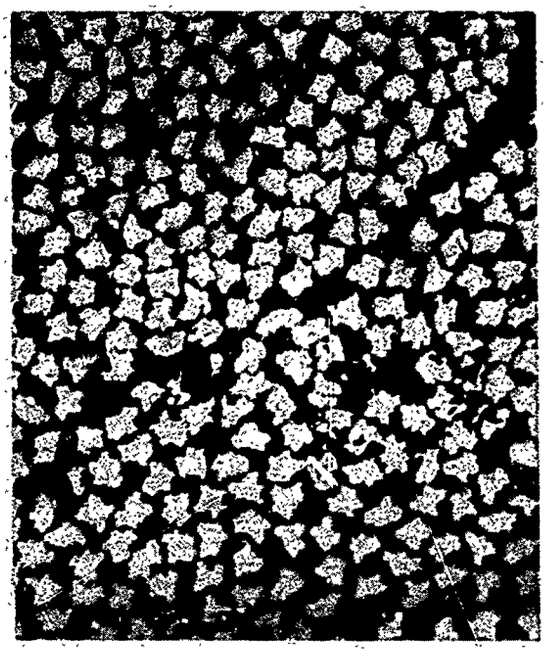


FIG. 21. VCK Fibers of Virgin Specimen 4P (500X).

FIG. 22. VCK Fiber, 816°C Lab. Char Specimen 4C (500X).

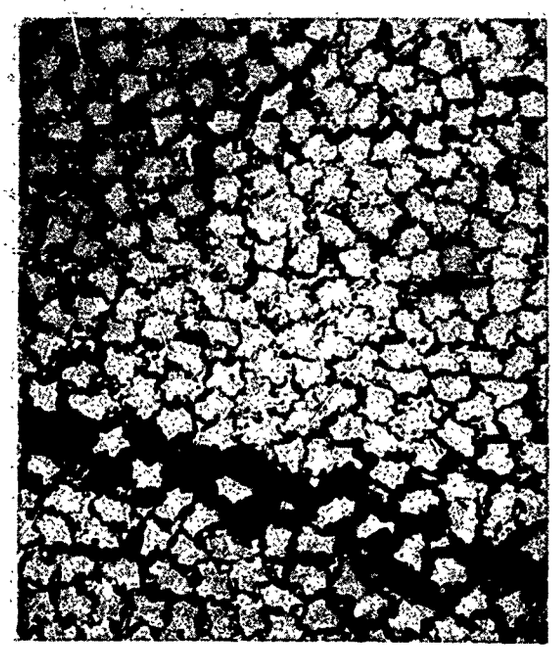


FIG. 23. WCA Fiber, Virgin Specimen 1BB After 810°C in K Apparatus (500X).

CONCLUSIONS

Conclusions drawn from observations made on graphite cloth phenolic and carbon cloth phenolic specimens evaluated are as follows:

1. Orientation of the reinforcing fabric with respect to heat flow direction has the greatest influence on thermal conductivity of those parameters investigated. Thermal conductivity is highest in the with-ply direction and is two to five times greater than that in the across-ply direction.

2. Fibers with a high thermal conductivity relative to the matrix resin act as channels of least resistance and direct heat flow along the fiber. Reinforcing fibers influence thermal conductivity in the with-ply direction in proportion to their thermal conductivity.

3. Thermal conductivity of the reinforcing fiber has a much lesser influence on thermal conductivity in the across-ply direction and is overshadowed by influences of other parameters such as specimen density, resin content, and relative conductivity of the virgin or charred resin.

4. Charred laminates generally, but not always, have a higher thermal conductivity than virgin laminates. The additional conductivity of charred over the virgin resin is a contribution of the matrix and acts as a constant value at a given temperature and resin content, so that its influence is high when the reinforcing fiber has a low conductivity or is in the across-ply direction. Its influence is low when the fiber has a high conductivity, especially in the with-ply direction.

5. The influence of molding pressure is not understood. Normally a higher molding pressure results in a laminate with a higher density because of the lesser void content where resin content is held constant. The lesser void content should contribute a small amount to a higher thermal conductivity. Whether a high pressure causes a further impregnation of the fiber with resin or better contact at the fiber resin interface to enhance heat transfer between the resin and fiber was not investigated, and its influence is not understood.

6. All virgin laminates investigated charred considerably between 300 and 550°C or higher. During resin degradation, gases are evolved which carry off heat and make it unavailable for heat transport. The dip in the conductivity curves between 300 and 550 degrees is a false value of thermal conductivity because a true steady-state condition has not been attained in that dynamic resin decomposition is occurring due to temperature, even though guard heaters have been adjusted to steady-state conditions as indicated by monitoring thermocouples. The same process occurs in pre-charred laminates. The effect is small until the pre-char temperature is reached, then becomes pronounced in some laminates depending on their time-temperature history.

7. The value of α in the equation $K_\theta = K_{90} (1 + \alpha \cos \theta)$ is different for each laminate investigated. It appears to be temperature dependent but should be investigated to higher temperatures to prove the validity of its temperature dependence.

8. The cut-bar thermal conductivity apparatus used is not adequate for determining thermal conductivity of specimens oriented at angles differing appreciably from 0 and 90 degrees.

Appendix

The TC 200 thermal conductivity apparatus was chosen for this study because it could utilize a small specimen, gives fairly accurate data, has a high temperature range, and achieves steady-state conditions fairly rapidly. Once guard heater settings are known, a minimum of 2 hours is required between readings at 100 to 200°C intervals. Changing specimens required 1 1/2 hours and changing standards another 1 1/2 hours. Heat-up time to the first temperature was generally 4 hours as was cool-down time from the maximum temperature.

A cross section of the thermal conductivity apparatus is shown in Fig. A1 which is a cutaway of the portion shown in Fig. 2 with the guard heater tower in the up position. Heat flows from the top heater, A, through platinum foil into the top standard, G; through foil and into the specimen, through foil into the bottom standard, G; then again through foil and into the bottom heater, I, which is at a lower temperature and therefore the heat sink. The central column is surrounded by insulation, guard heaters, and then more insulation.

Temperatures within the standards and specimen were taken at 1/2 hour intervals (TCs 8 through 13). Guard heaters (B through H) were then adjusted as required to attain 1°C or less ΔT between TCs 1 and 13 and 7 and 8 while TCs 2 through 6 monitored ΔT between average temperatures for pairs of corresponding TCs 8 through 13. When steady-state was achieved by maintaining a ΔT of 1°C or less on paired and averaged TCs, the TC output was recorded to the nearest microvolt. A steady-state condition must be maintained for 1/2 hour to prove steady-state conditions before moving on to the next evaluation temperature 100 or 200°C higher.

Contact pressures at specimen, standard, and heater interfaces were preset at 15 to 20 pounds force by means of a spring loaded pressure foot. Thermal expansion of the central column during heat-up is taken up by a spring. Hopefully the spring is long enough so the force will not exceed 25 pounds. Some specimens decreased in length due to charring and plastic flow while under an axial force; therefore, less than 15 pounds force was sustained after cool-down.

Water ducts in the bottom steel plate carried off excess heat to help maintain the bottom heater as a heat sink and keep the electrical units below the plate within tolerances. Water pumped through these ducts was maintained at a constant temperature by means of a thermostatically controlled refrigeration unit.

A sample data sheet is shown in Fig. A2. Voltages from TCs 8 through 13 were recorded on the left side and averaged. Voltages from TCs 1 through 7 were recorded at the right side of the central column. The voltage for TC 13 was 817 microvolts and agreed with that for TC 1 by

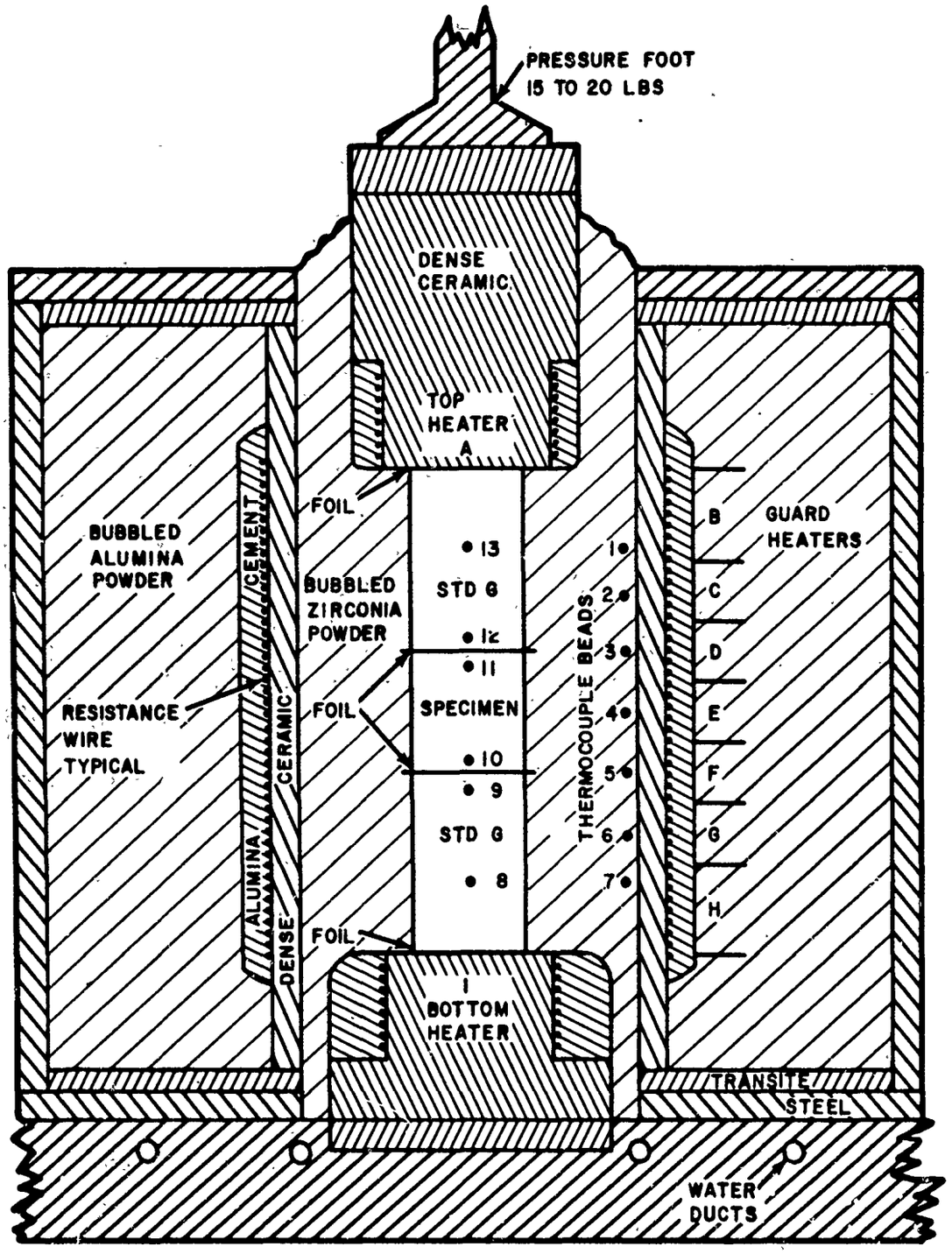


FIG. A1. Cross Section of Thermal Conductivity Apparatus.

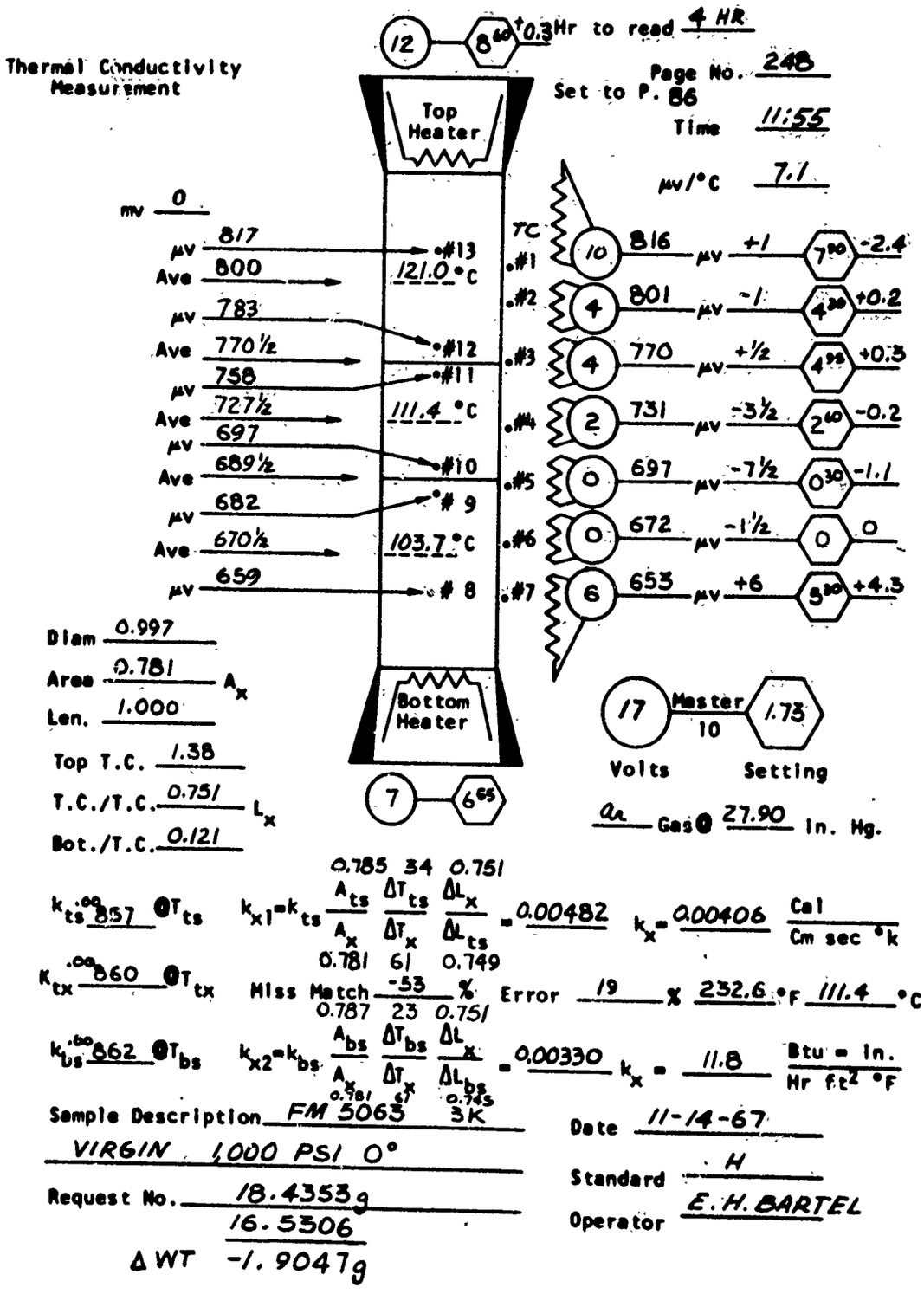


FIG. A2. Sample Data Sheet for Specimen 3K.

1 microvolt. The greatest disagreement was for TC 5 which was 7 1/2 microvolts lower than the average of TCs 9 and 10 so that TC 6 was slightly greater than 1°C (7.1 μv/°C) lower, but close enough to ±1°C for steady-state conditions. Circles contain voltages supplied to their respective heaters and hexagons contain the setting of the rheostat dial. Numbers at the extreme right are variations applied to the rheostat setting for the next higher temperature. Temperatures were recorded only for the average TC voltages of the top standard, specimen and bottom standard.

The K values of the standard were obtained from a table for each temperature and recorded at the lower left side of Fig. A2 (K_{ts} = thermal conductivity of top STD H in cal/cm sec °C at the temperature of the top STD, etc.). Values of cross-sectional area (Ax), thermocouple spacing (ΔLx), and temperature drop (ΔT_{ts}) across top STD and specimen (ΔTx) were multiplied by K_{ts} to obtain the K value of specimen X compared to the top standard. The same process was repeated for the bottom standard and the results averaged for a final K value of the specimen.

Thermal conductivity values are published with various units in the literature; therefore, conversion factors are given in Table A1 for convenience.

TABLE A1. Thermal Conductivity Conversion Factors.

		Metric			English					
		$\frac{\text{Watt}}{\text{cm °K}}$	$\frac{\text{cal}}{\text{sec cm °K}}$	$\frac{\text{k cal}}{\text{hr m °K}}$	$\frac{\text{Watt}}{\text{in °R}}$	$\frac{\text{Btu}}{\text{hr in °R}}$	$\frac{\text{Btu in}}{\text{hr ft}^2\text{ °R}}$	$\frac{\text{Btu}}{\text{sec in °R}}$	$\frac{\text{Btu}}{\text{ft sec °R}}$	$\frac{\text{Btu}}{\text{hr ft °R}}$
Metric	$1\ \frac{\text{Watt}}{\text{cm °K}} =$	1	0.2390	86.04	1.411	4.815	693.4	1.337×10^{-3}	0.01605	57.78
	$1\ \frac{\text{cal}}{\text{sec cm °K}} =$	4.184	1	360	5.904	20.15	2901	5.596×10^{-3}	0.06716	241.8
	$1\ \frac{\text{k cal}}{\text{hr m °K}} =$	0.011622	2.778×10^{-3}	1	0.016400	0.05596	8.058	1.5545×10^{-5}	1.865×10^{-4}	0.6715
English	$1\ \frac{\text{Watt}}{\text{in °R}} =$	0.7087	0.1694	60.97	1	3.412	491.4	9.478×10^{-4}	0.01137	40.946
	$1\ \frac{\text{Btu}}{\text{hr in °R}} =$	0.2077	0.04964	17.87	0.2931	1	144	2.778×10^{-4}	3.333×10^{-3}	12
	$1\ \frac{\text{Btu in}}{\text{hr ft}^2\text{ °R}} =$	1.442×10^{-3}	3.447×10^{-4}	0.12409	2.035×10^{-3}	6.944×10^{-3}	1	1.929×10^{-6}	2.315×10^{-5}	0.08333
	$1\ \frac{\text{Btu}}{\text{sec in °R}} =$	747.7	178.70	6.433×10^{4}	1,055	3600	5.184×10^{5}	1	12	43,200
	$1\ \frac{\text{Btu}}{\text{ft sec °R}} =$	62.31	14.89	5,361	87.92	300	43,200	0.08333	1	3,600
	$1\ \frac{\text{Btu}}{\text{hr ft °R}} =$	0.01731	4.136×10^{-3}	1.4891	0.02442	0.08333	12	2.3148×10^{-5}	2.778×10^{-4}	1

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13. ABSTRACT

Thermal conductivity values of fabric-reinforced laminates are reported for virgin and charred laminates. Data are presented graphically from 100 to 1100°C. Two types of graphite cloth and two types of carbon cloth were investigated as laminate reinforcements at angles of 0 and 90 degrees to heat flow direction. Parameters of molding pressure, char temperature, and additional orientations at 30 and 60 degrees were investigated for one type of laminate. Two specimens taken from a fired rocket motor ablative chamber were evaluated and compared to a laboratory counterpart.

Fabric orientation with respect to heat flow direction was found to have the greatest influence on thermal conductivity in laminates.

A discussion is presented to explain the decrease in thermal conductivity when charring of the laminate resin occurs.

A comparative cut-bar thermal conductivity apparatus was used to obtain values of thermal conductivity with a fairly high degree of confidence.

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